

Li-doped Ionic Liquid Electrolytes

From Bulk Phase to Interfacial Behavior



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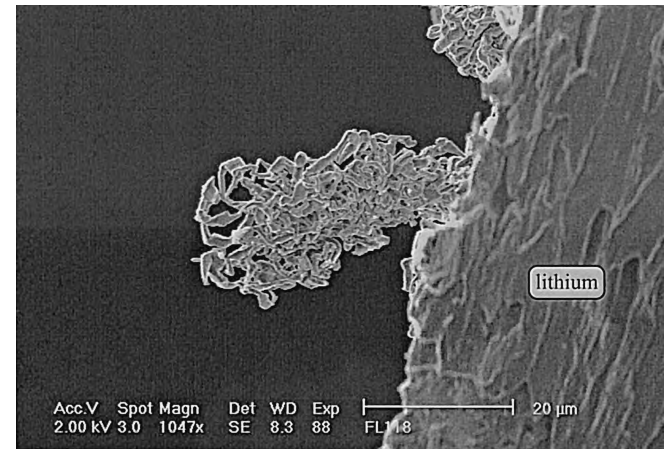
Army Research Center

Oleg Borodin

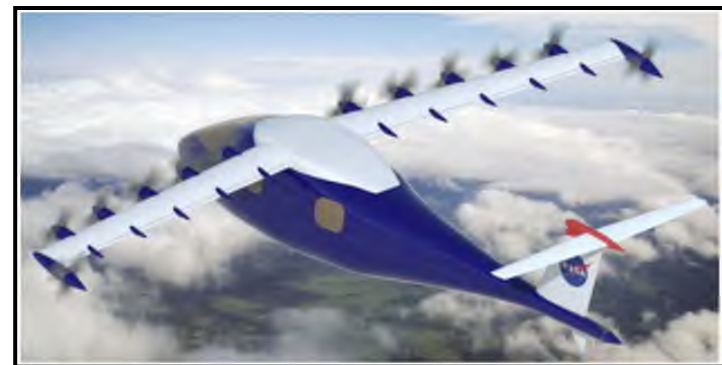
Ionic liquids for electrochemical applications



- **Advanced electrodes:** help stabilize cycling against Li-metal
- **Li-ion batteries:** possible safer alternative to organic electrolytes
- **Supercapacitors:** double layer capacitor electrolyte
- **Electrodeposition:** wide electrochemical window solvent
- **Biofuel cells:** replace water as more stable solvent

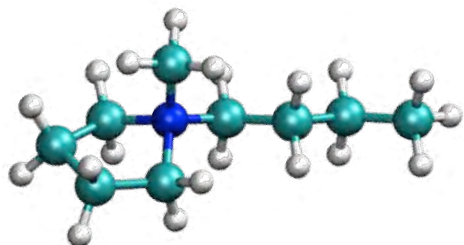


F. Orsini et al., J. Power Sources 76, 19-29 (1998)

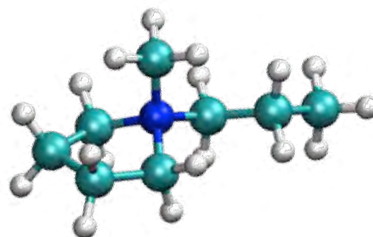


NASA Electric Aircraft

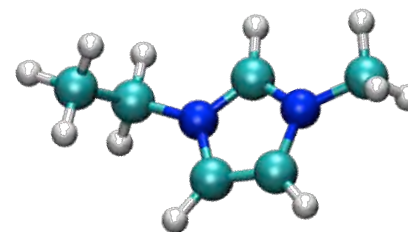
Ionic liquids (ILs)



[pyr14][TFSI]



[pyr13][FSI]



[EMIM][BF₄]

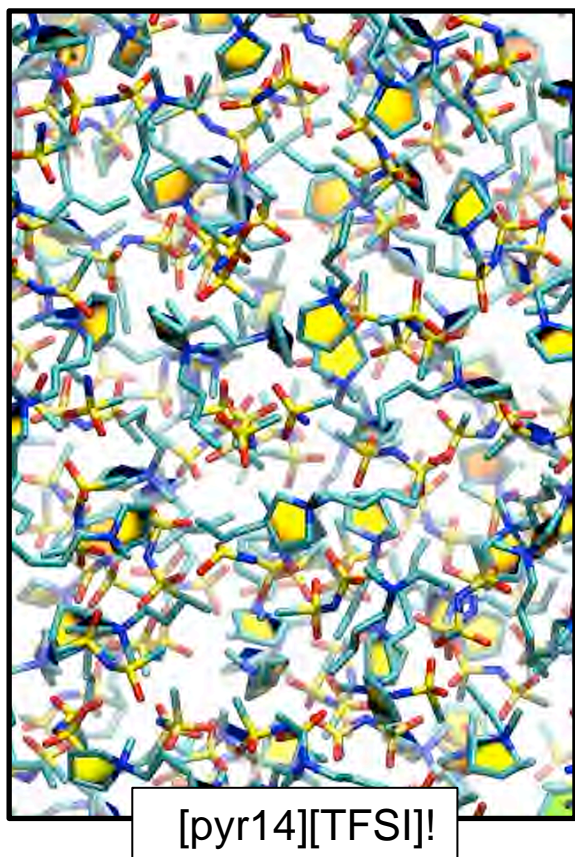
C (green)
N (blue)
S (yellow)
O (red)
F (purple)
B (pink)
H (white)

Chosen for suppression of dendrites on Li⁺ metal anodes!

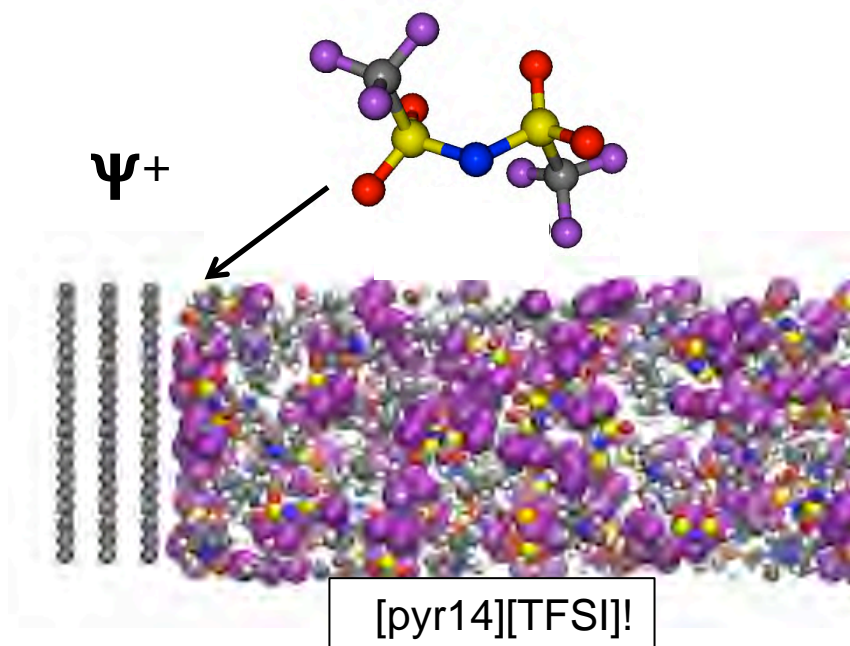
Bhattacharyya et al., Nature Mater. (2010)
Basile, et al., Electrochem. Commun. (2013)

Computational Study of Li-doped ILs with Experimental Validation

Bulk Properties

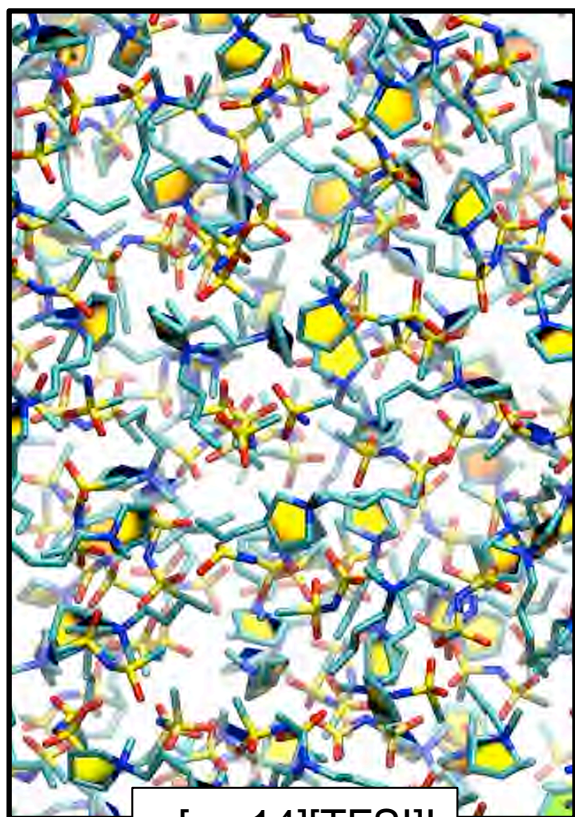


Interfacial Properties



Computational Study of Li-doped ILs with Experimental Validation

Bulk Properties

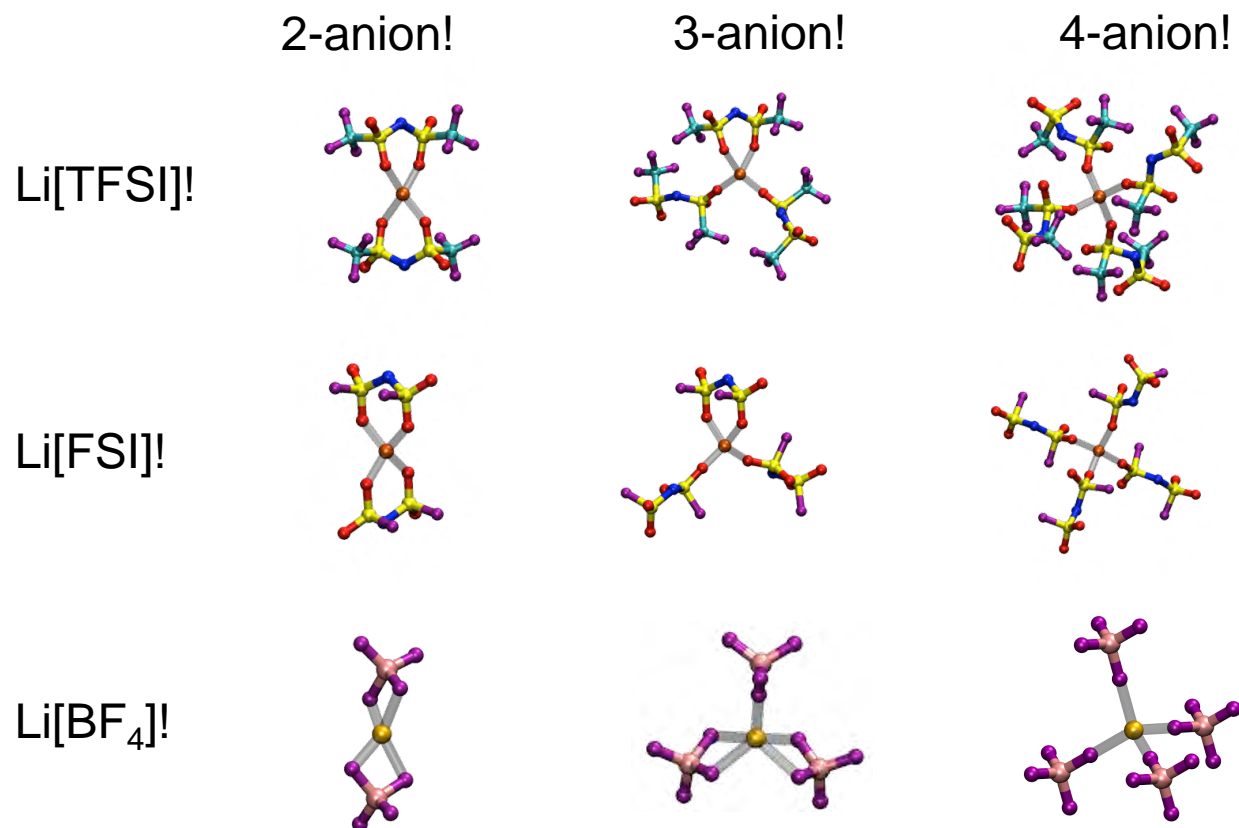


[pyr14][TFSI]!

- **Quantum chemistry (QC) of Li/Anion clusters:**
 - Li solvation structure/energetics
 - IR/Raman spectra
 - electrochemical windows
- **DFT-MD simulation of Li-doped liquid:**
 - Li solvation structure
 - IR spectra
 - electrochemical windows
- **Polarizable-MD (APPLE&P) simulation of Li-doped liquid:**
 - Li network structure
 - transport properties
 - transport mechanisms

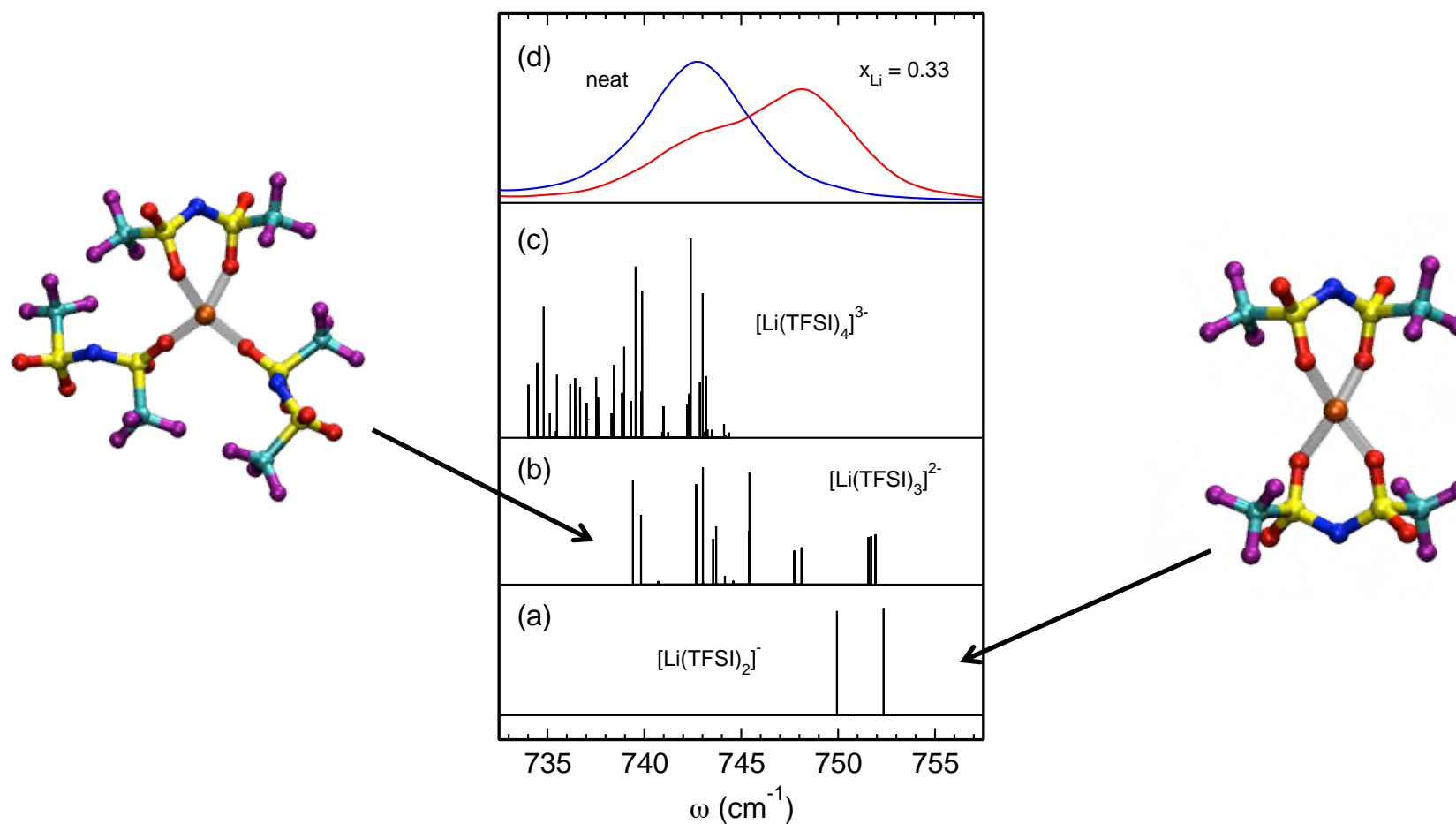
O. Borodin, *J. Phys. Chem. B* **113**, 11463 (2009)
J.B. Haskins, et al., *J. Phys. Chem. B* **118**, 11295 (2014)
C.W. Bauschlicher, et al., *J. Phys. Chem. B* **118**, 10785 (2014)
J.B. Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)

Stable solvation shells of Li^+ (QC Clusters)



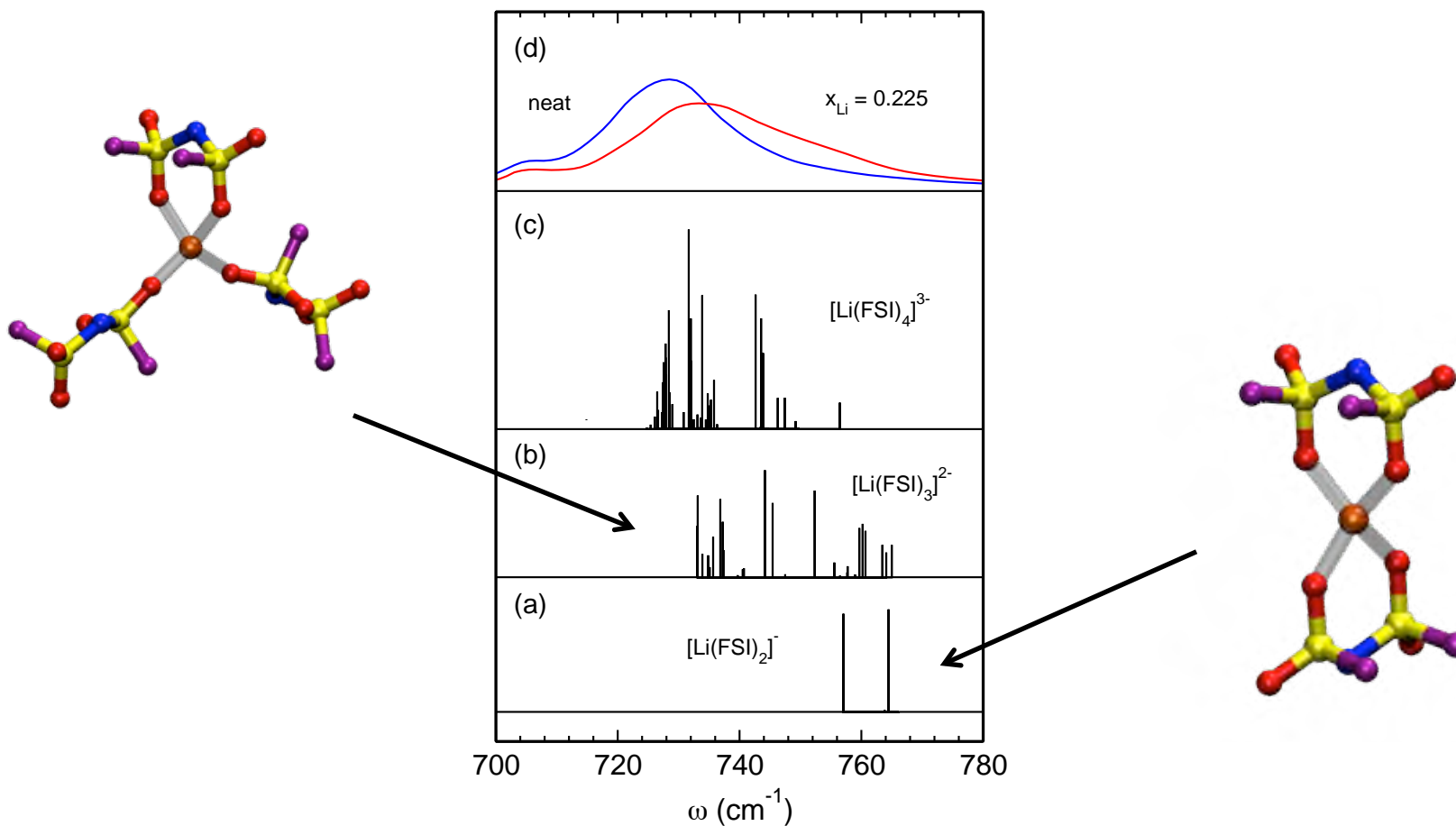
Many potential 2, 3, and 4 anion Li^+ solvation shells !

Raman analysis of Li[TFSI] (QC Clusters)



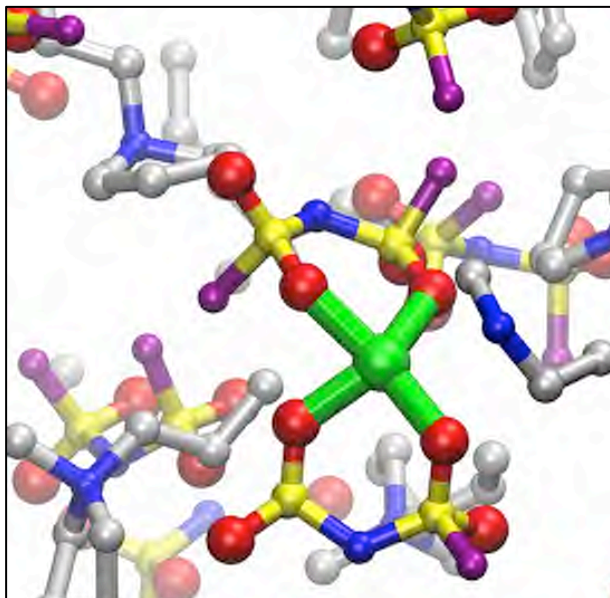
2 and 3 [TFSI] coordination are shifted!

Raman analysis of Li[FSI] (QC Clusters)

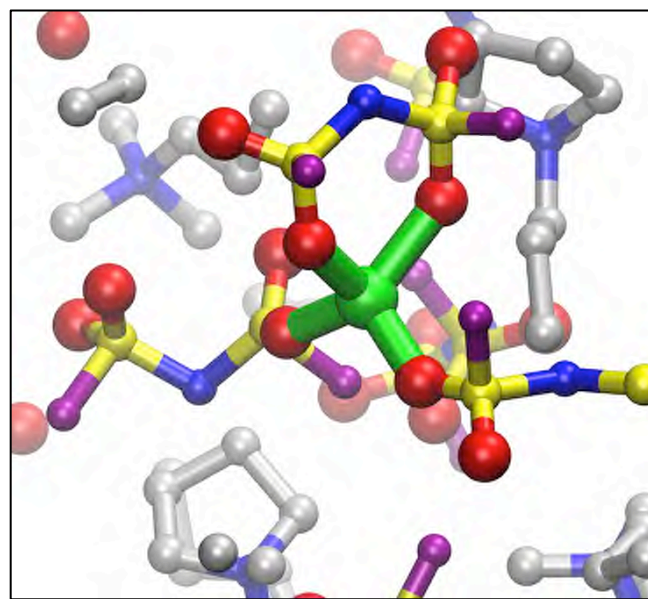


2 and 3 [FSI] coordination are shifted!

Li solvation shell stability (DFT-MD Liquid)

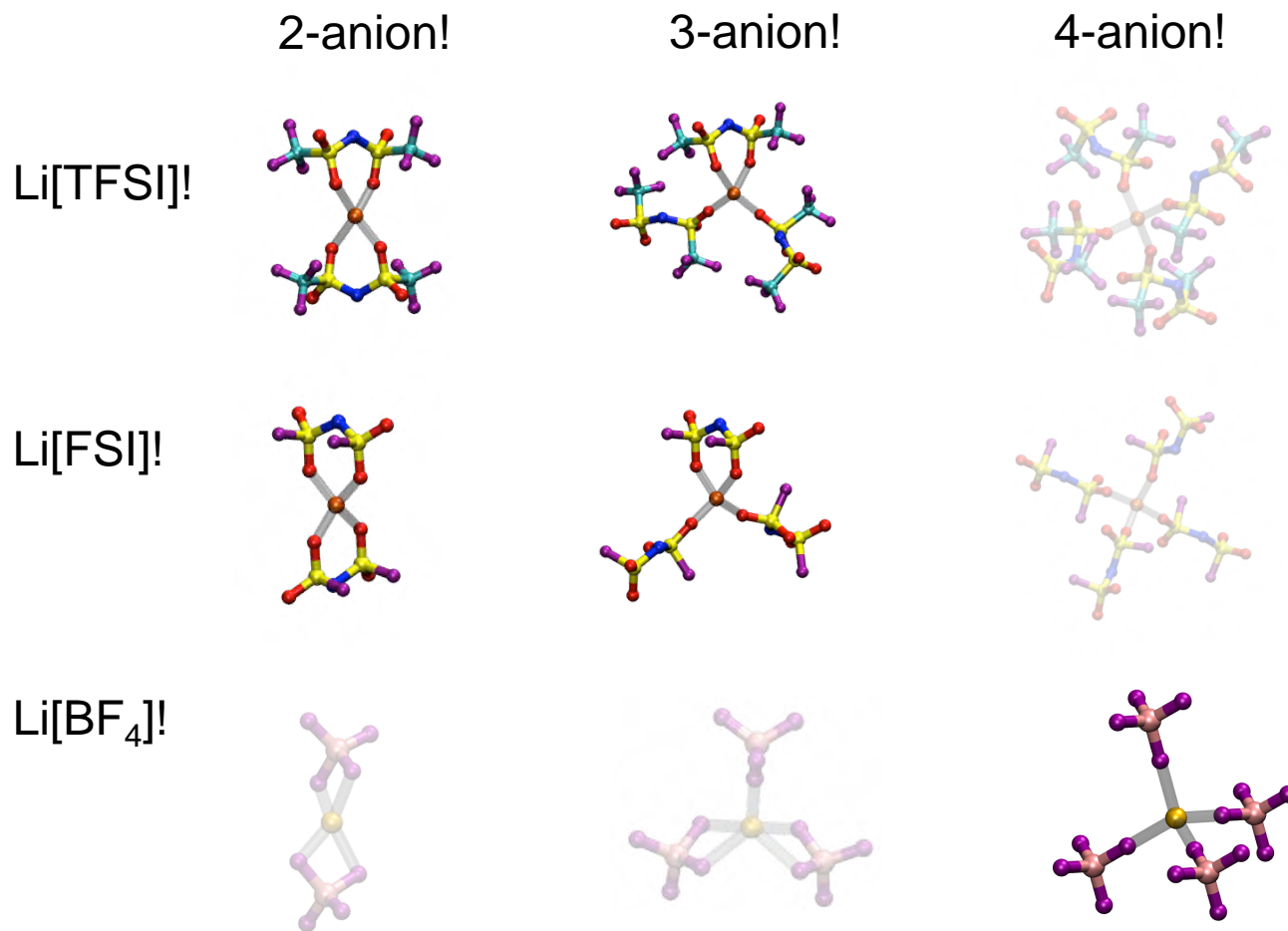


20-100 ps; 12-16 pairs; $T = 363 \text{ K}$



Highly unfavorable configurations exchange anions within 20 ps!

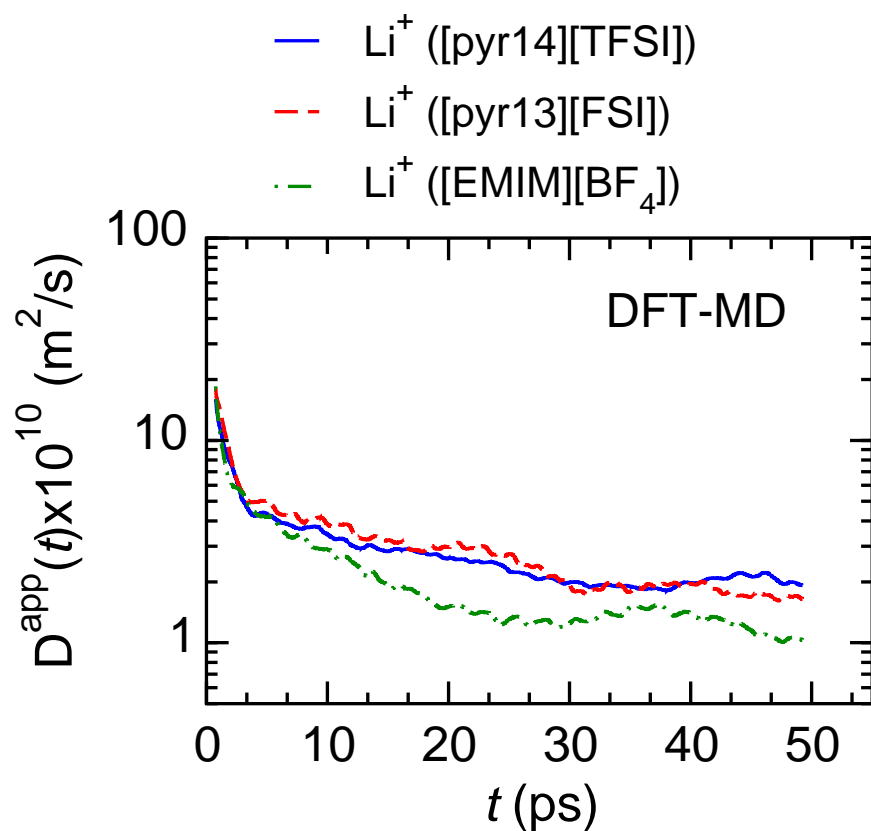
Stable solvation shells of Li^+ (DFT-MD Liquid)



2, 3 anion Li^+ solvation shells for TFSI/FSI!
4 anion Li^+ solvation shell for BF_4 !



Li⁺ Diffusion coefficients (DFT-MD Liquid)



Diffusion Coefficients $\times 10^{10} \text{ (m}^2\text{/s)}$

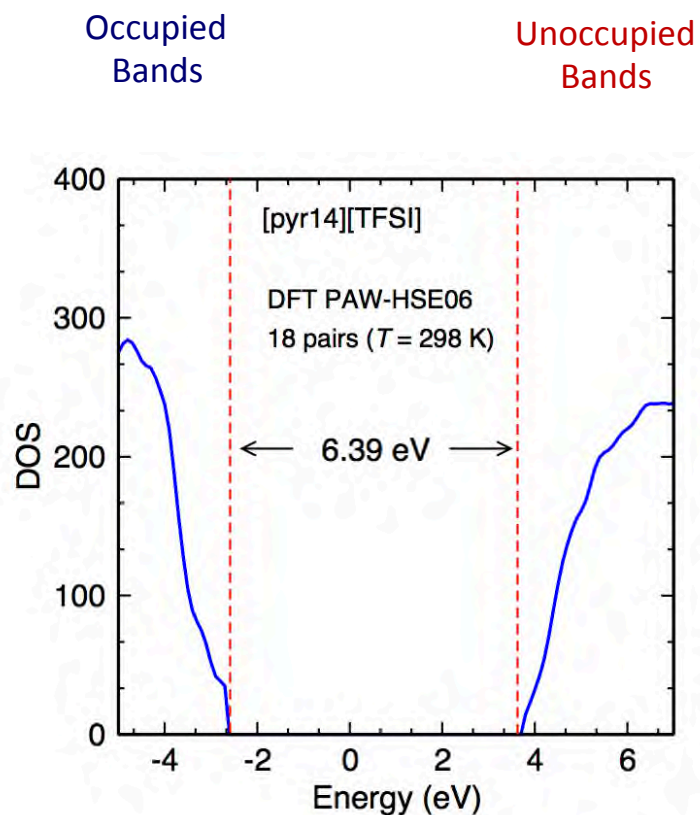
	DFT (50ps)	DFT (∞)	Exp.
[pyr14] [TFSI]	1.91	0.71	0.34
[pyr13] [FSI]	1.64	0.78	0.47
[emim] [BF ₄]	1.03	0.79	0.65

100+ ps; 8-12 pairs; T = 363 K

Diffusion from ~100 ps DFT-MD order of magnitude agreement with experiment!



Electrochemical windows (DFT-MD Liquid)



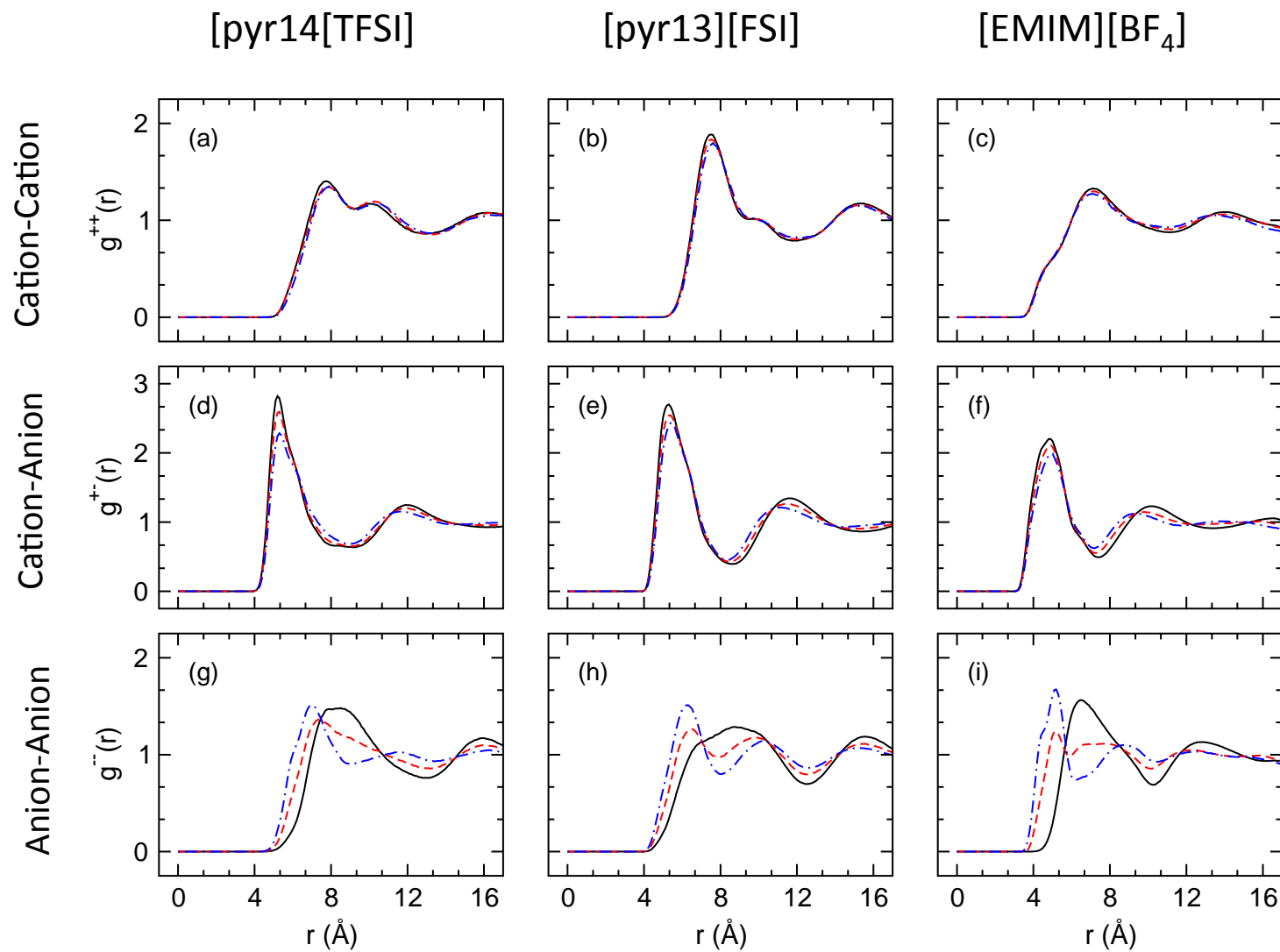
Electrochemical Windows (eV)

	DFT (PBE)	DFT (HSE06)	Exp.
[pyr14][TFSI]	4.6	6.5	3.8-6
[pyr13][FSI]	4.7	6.7	4.3-6
[EMIM][BF ₄]	3.9	5.4	4.3

10 PFF-MD configurations; 24 pairs; $T = 298$ K

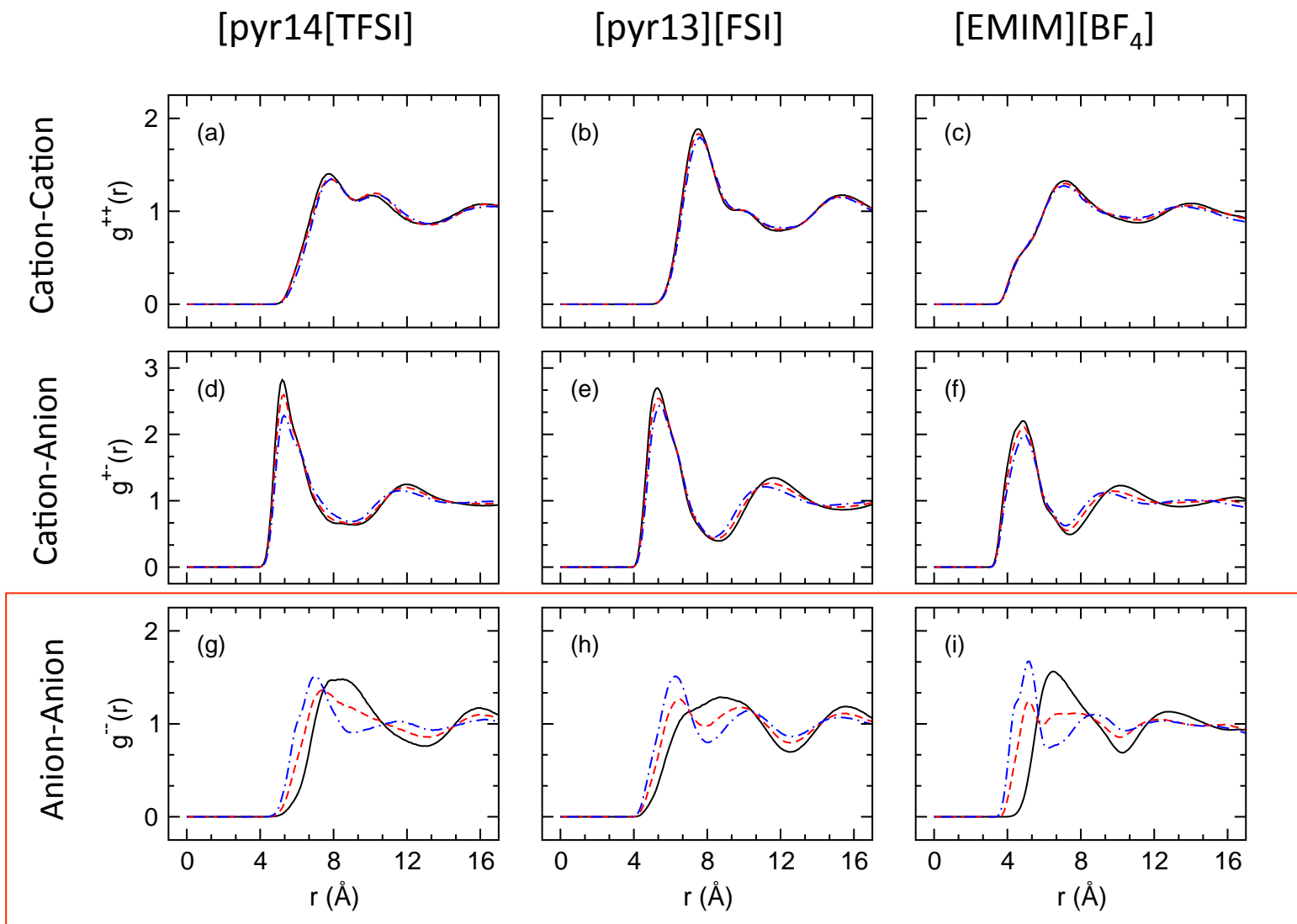
Electrochemical window of liquids with pure and hybrid functionals bounds experiment!

Radial distribution functions (PFF-MD)



144-216 pairs

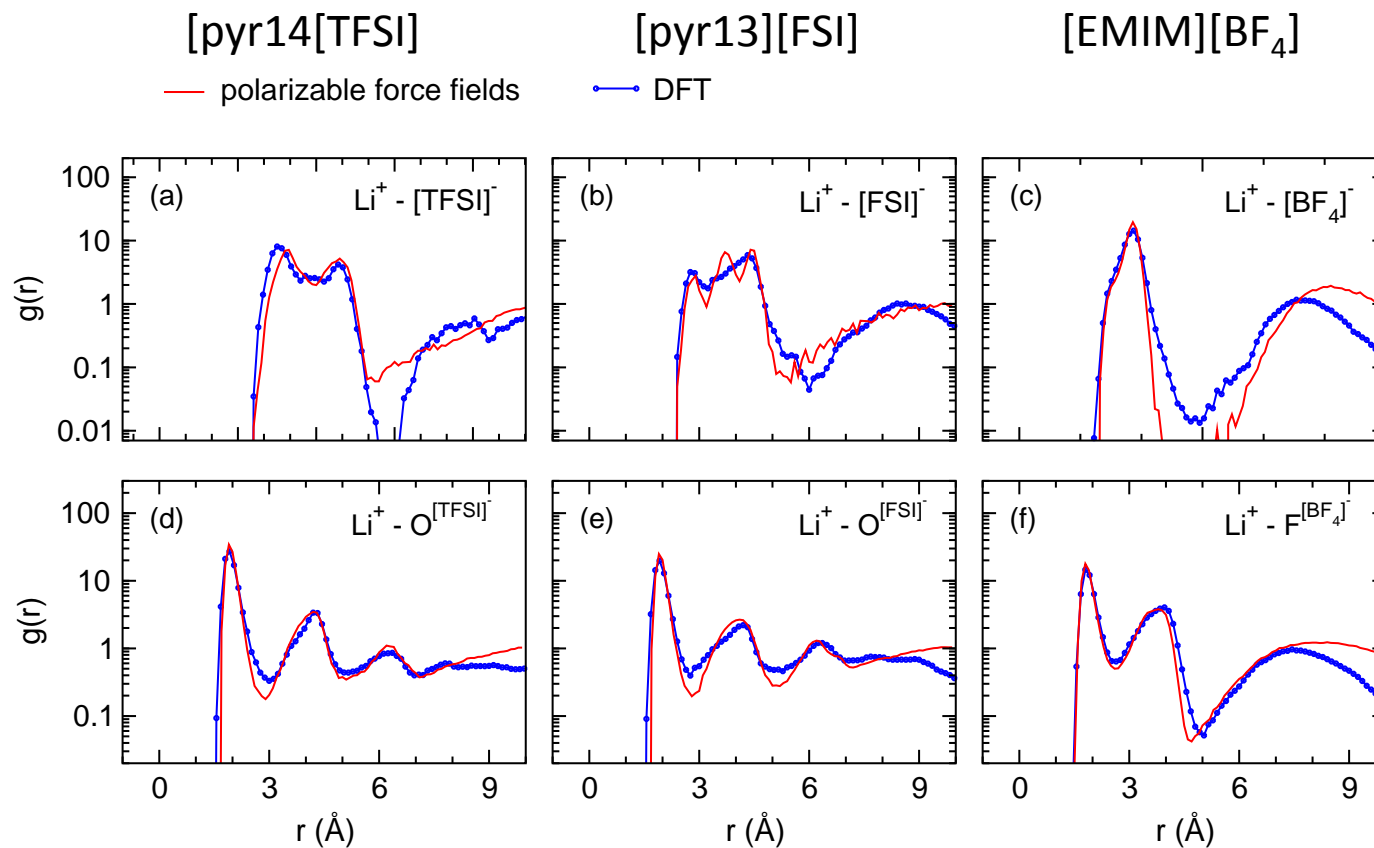
Radial distribution functions (PFF-MD)



144-216 pairs



High accuracy comparison (PFF-MD)

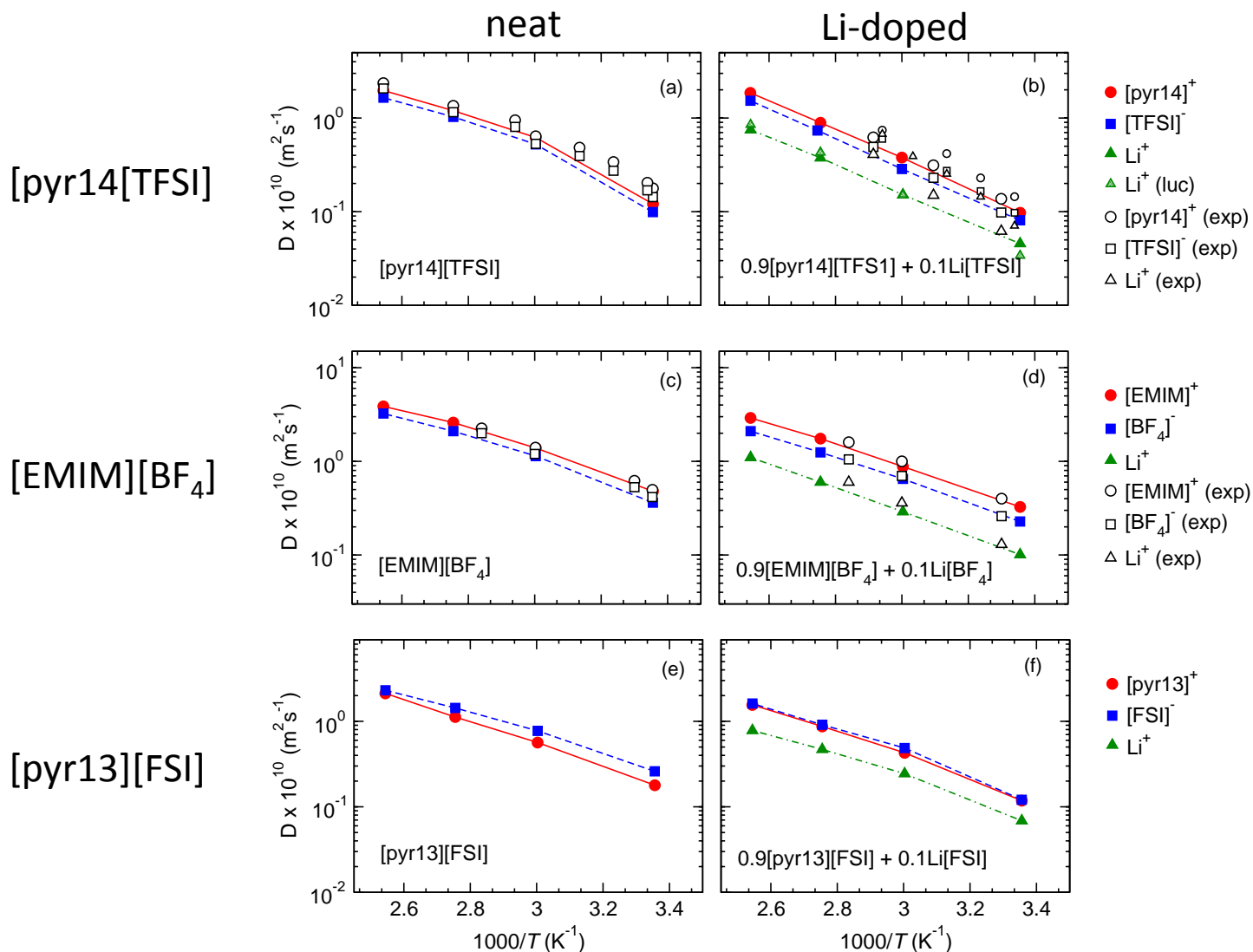


8-12 pairs; $T = 363 \text{ K}$

PFF-MD radial distributions in good agreement with DFT-MD!

J.B. Haskins, et al., *J. Phys. Chem. B* **119**, 14705 (2015)
O. Borodin, *J. Phys. Chem. B* **113**, 11463 (2009)

Diffusion (PFF-MD)

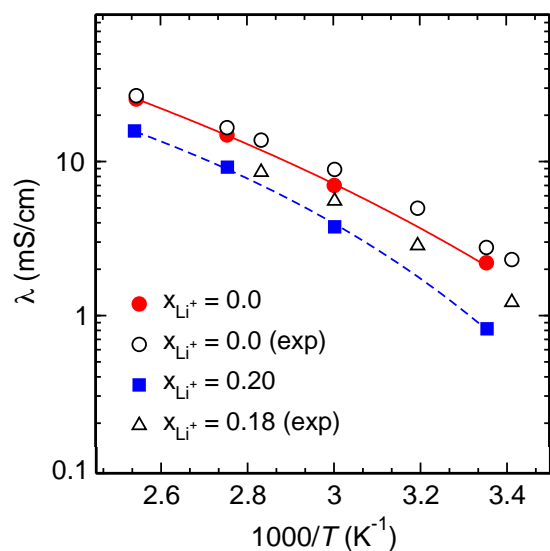


Li-doping suppresses diffusion of all ions!

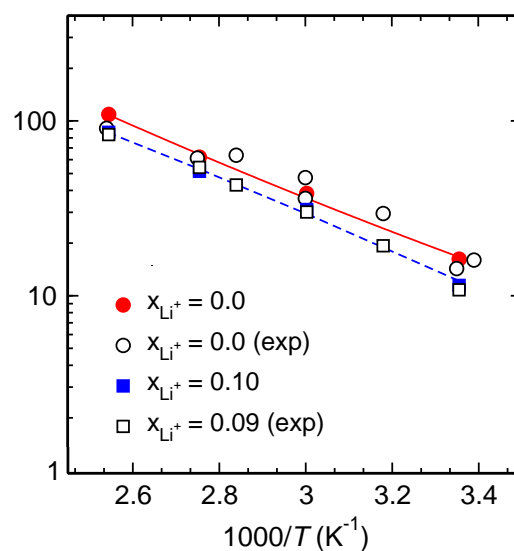
Ionic conductivity (PFF-MD)



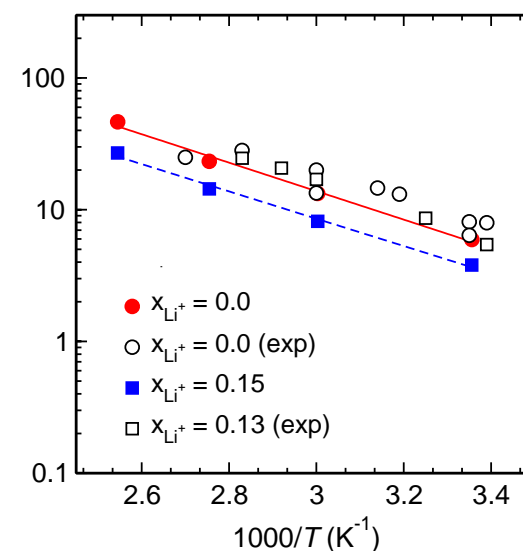
[pyr14][TFSI]



[EMIM][BF₄]

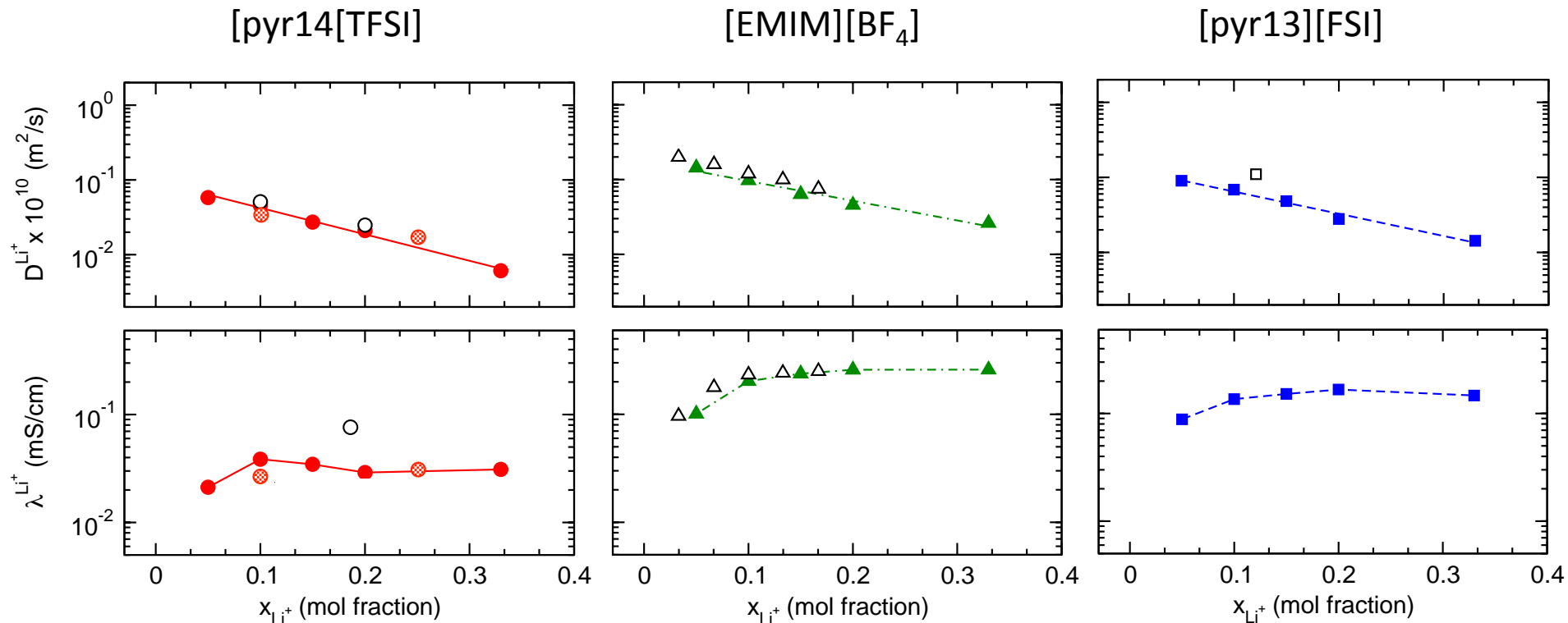


[pyr13][FSI]



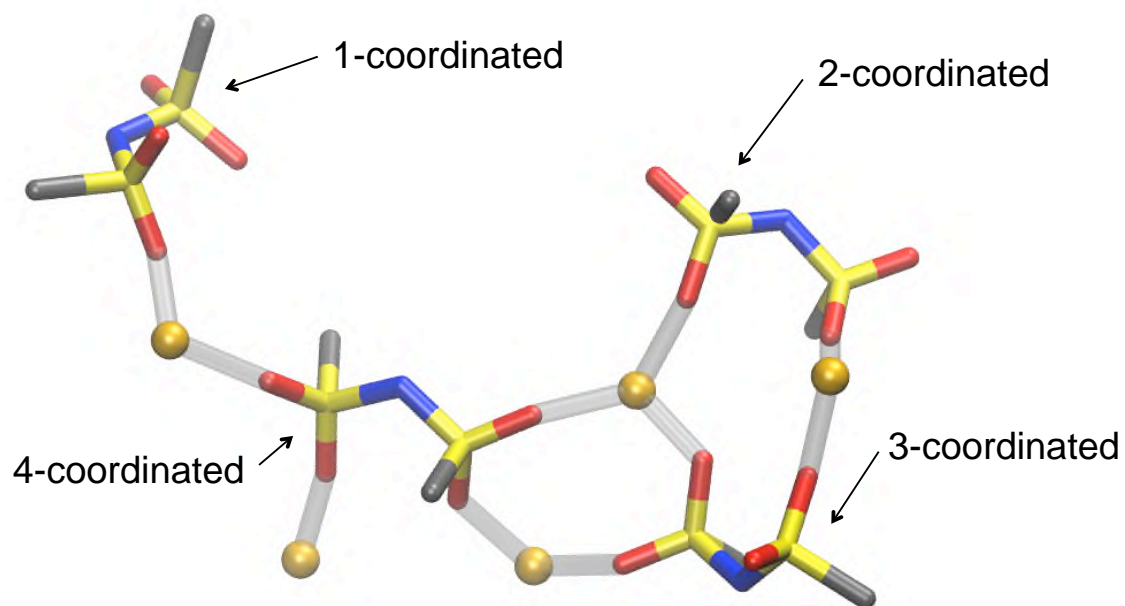
Li-doping suppresses conductivity of all systems!

Room-T Li transport (PFF-MD)



Li⁺ contribution to conduction plateaus at high salt doping!

Li⁺ ... Li⁺ networks (PFF-MD)

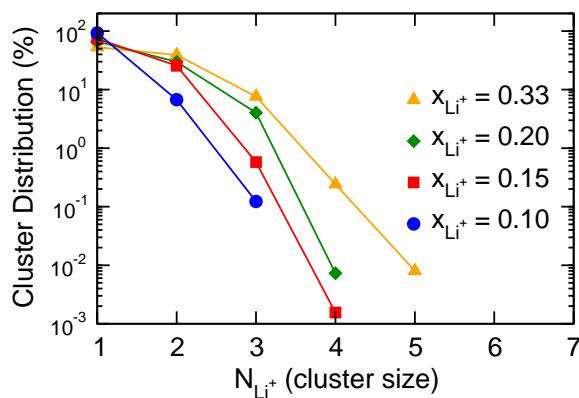


Network Li⁺ share bridging anions!

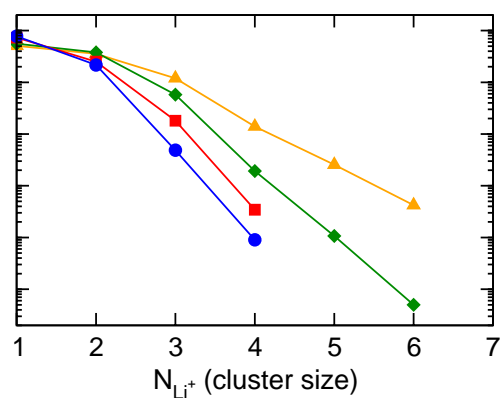
Li⁺ ... Li⁺ networks (PFF-MD)



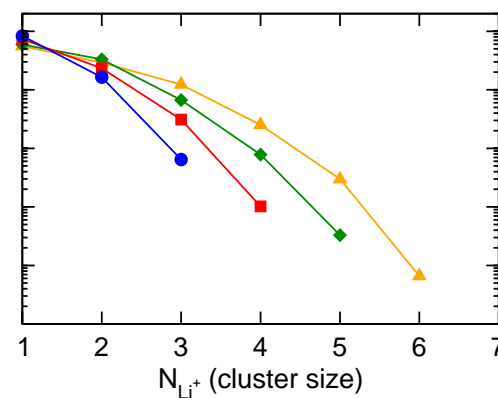
[pyr14][TFSI]



[EMIM][BF₄]



[pyr13][FSI]



Li⁺...Li⁺ networks present at all levels of doping!

Li⁺ ... Li⁺ networks (PFF-MD)



	x_{Li}	$\langle N_{\text{Li} \dots \text{Li}} \rangle$	$\langle n \rangle$	$\langle N_s^- \rangle / N_{\text{Li}}$
[pyr14][TFSI]	0.05	1.1	3.3	3.3
	0.15	1.4	3.3	2.8
	0.33	1.5	3.6	2.2
[pyr13][FSI]	0.05	1.1	3.8	3.7
	0.15	1.4	3.9	3.1
	0.33	1.6	4.0	2.5
[EMIM][BF ₄]	0.05	1.2	3.9	3.7
	0.15	1.4	3.9	3.2
	0.33	1.7	4.0	2.6

Apparent coordination decreases through Li-networks!

Room-T diffusion kinetics



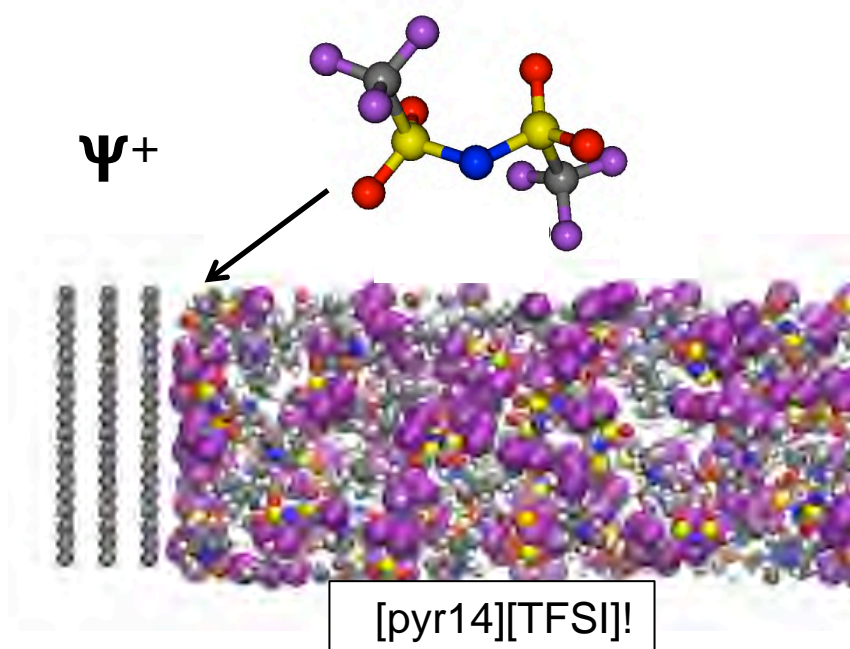
	[pyr14][TFSI]	[pyr13][FSI]	[EMIM][BF ₄]
x_{Li}	D_{veh}/D_{tot}	D_{veh}/D_{tot}	D_{veh}/D_{tot}
0.05	0.69	0.81	0.89
0.10	0.66	0.85	1.07
0.33	0.59	0.73	0.91

Vehicular mechanism dominates the diffusion and increases in importance with decreasing anion size !

Computational Study of Li-doped ILs with Experimental Validation

Interfacial Properties

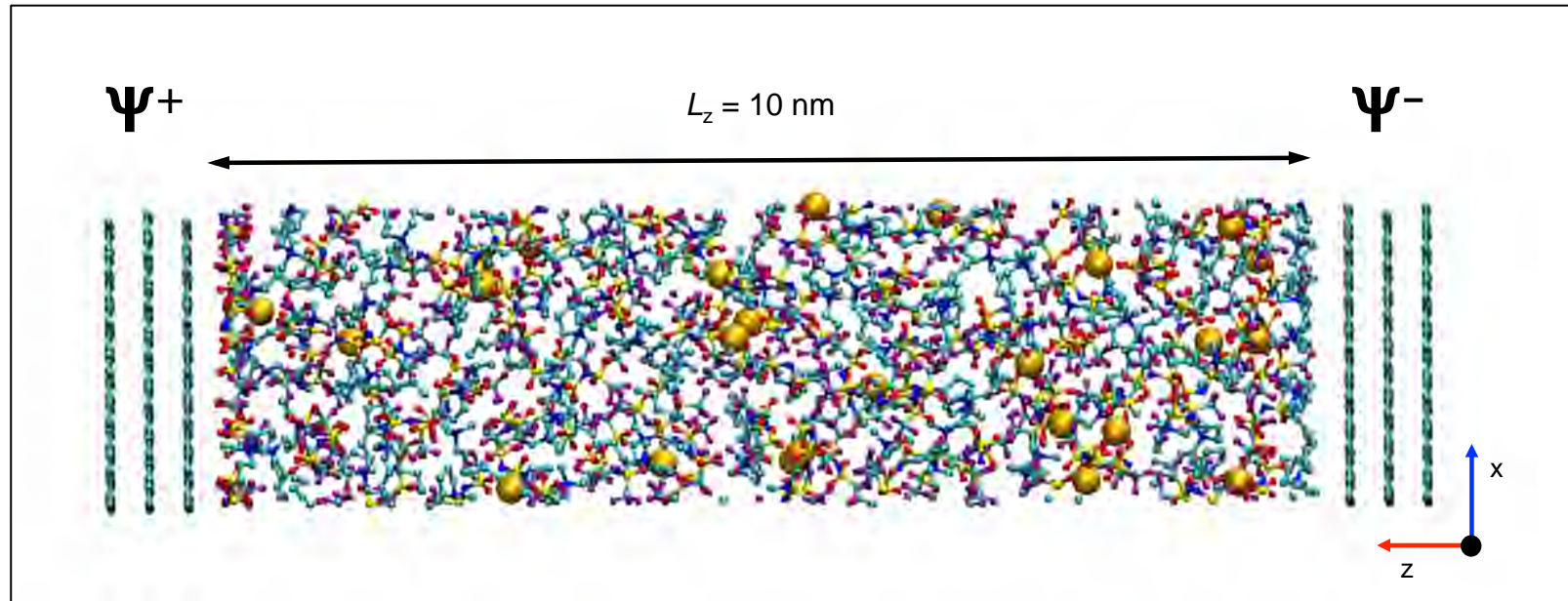
- Polarizable-MD for electrolytes
- Constant voltage electrodes
- Li^+ /EDL property analysis
 - structure
 - Li^+ solvation
 - differential capacitance
- Free energy analysis of Li^+ solvation



J.B. Haskins, et al., *J. Phys. Chem. C* (submitted)

J.B. Haskins, et al., *J. Chem. Phys.* (submitted)

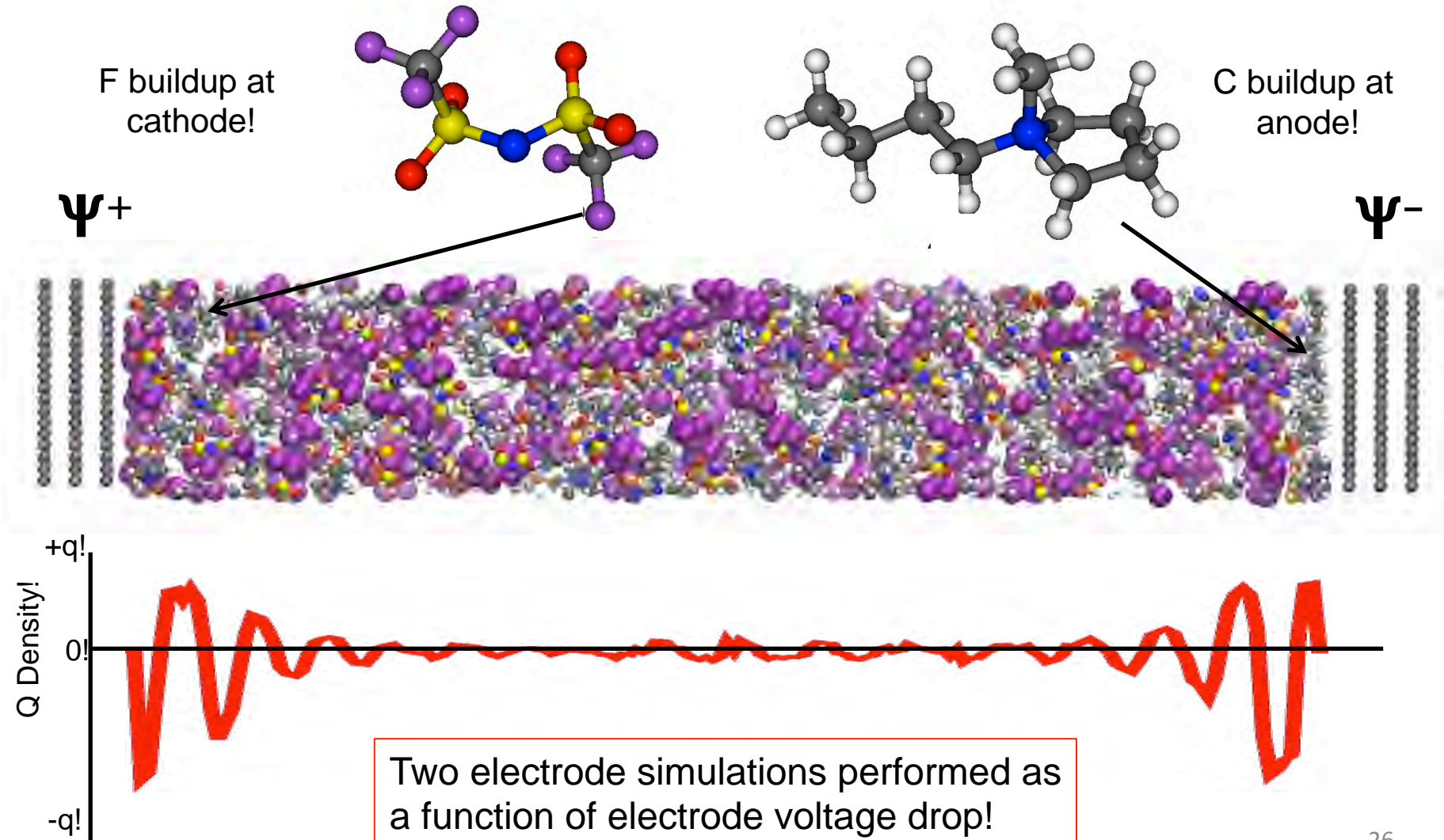
Interfacial Structure Simulations



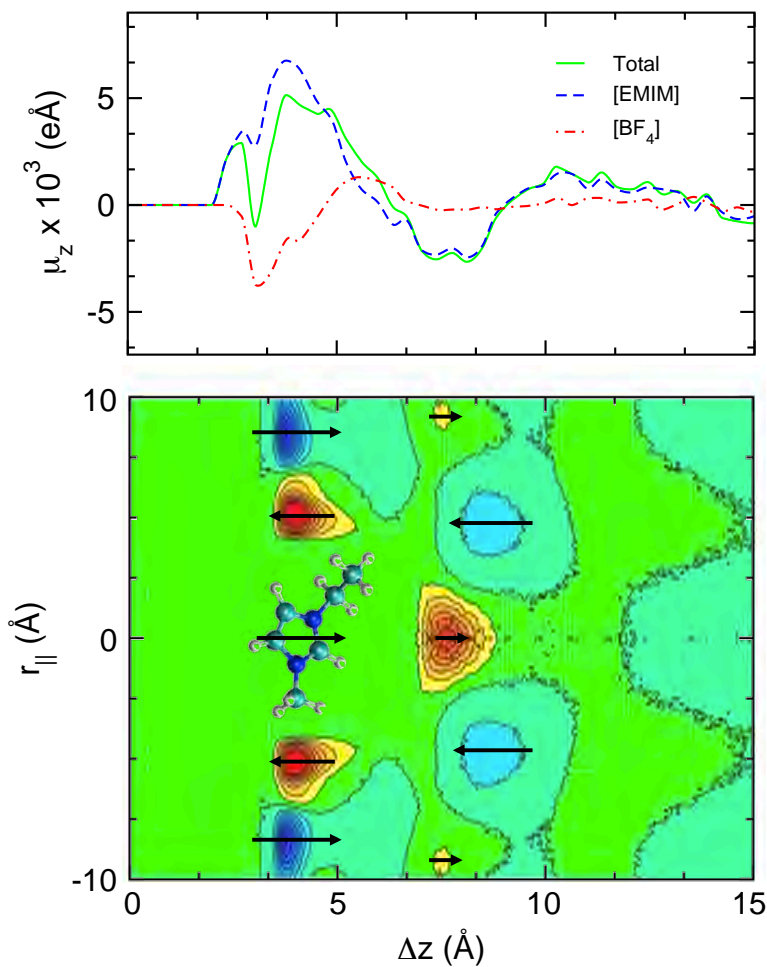
$$\Delta\Psi = \Psi^+ - \Psi^- = \text{constant}$$

Two electrode simulations performed as a function of electrode voltage drop!

Electric Double Layer (EDL)

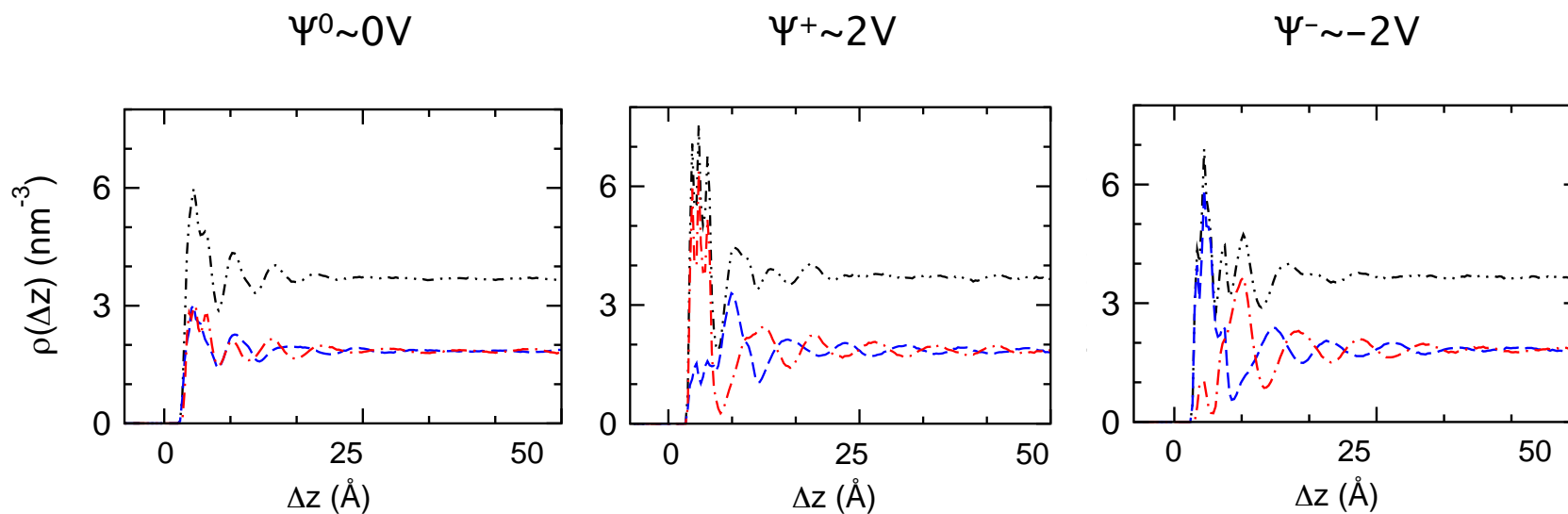


Polarization influence on the EDL



Polarization opposes formation of the EDL!

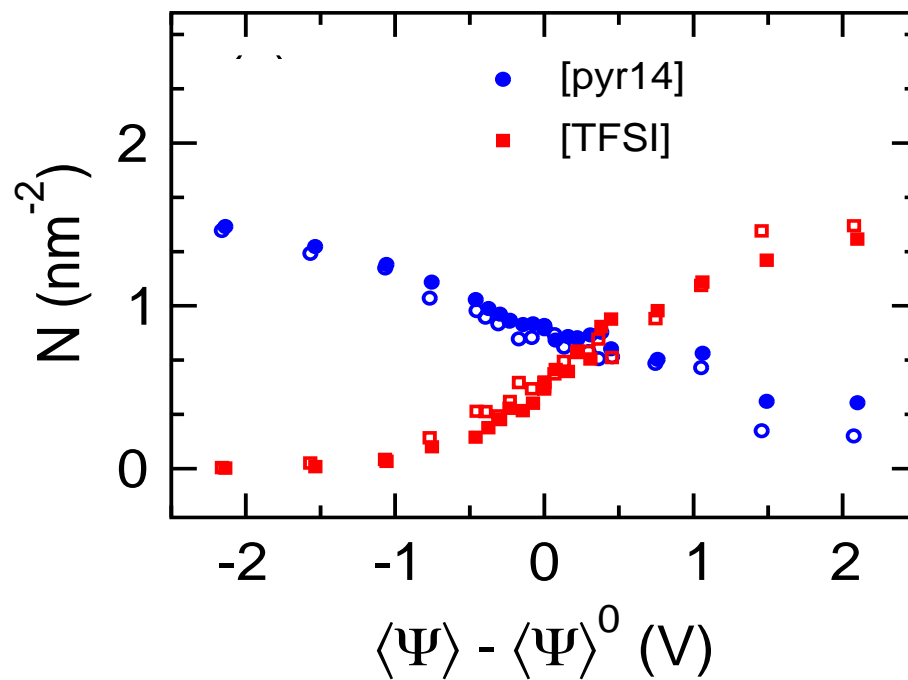
Ion density profiles: [pyr14][TFSI]



Black – total; Red – anion; Blue – cation

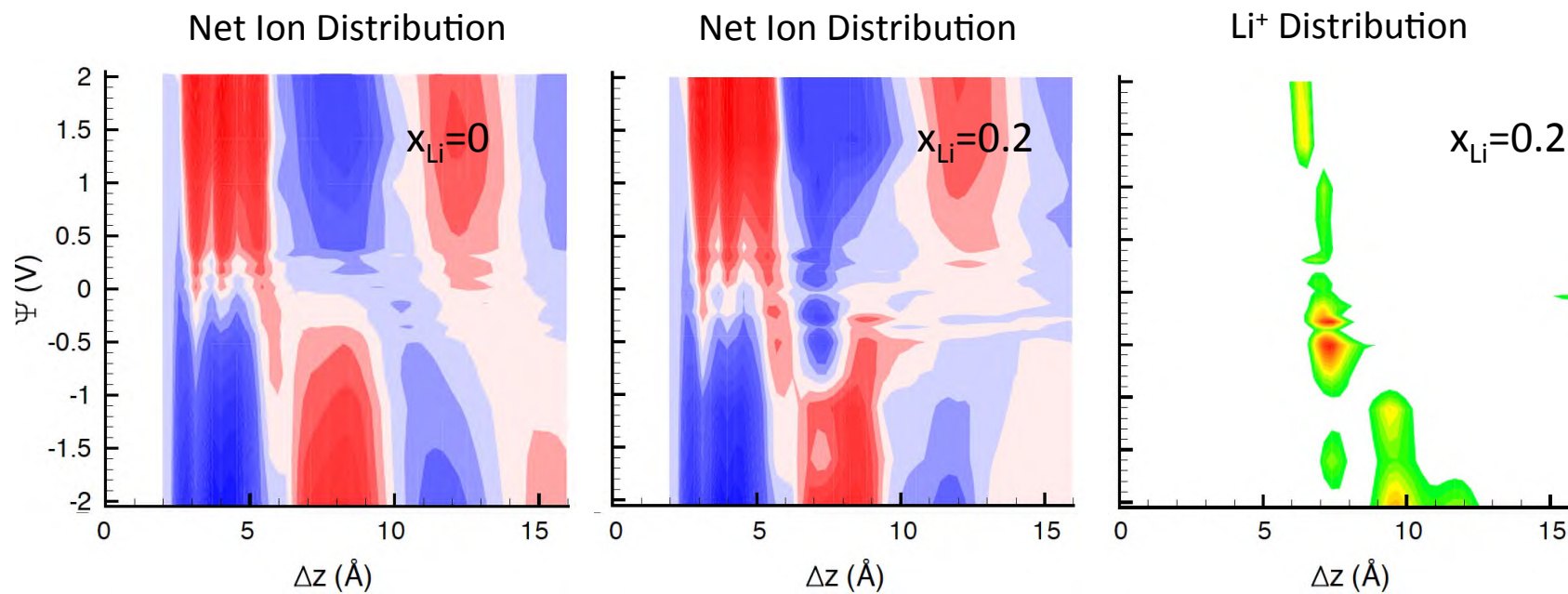
Complex layered structure at neutral and charged electrodes !

Ion accumulation at the surface: [pyr14][TFSI]



Ion depletion at high voltage!

Li⁺ influence on the EDL: [pyr14][TFSI]

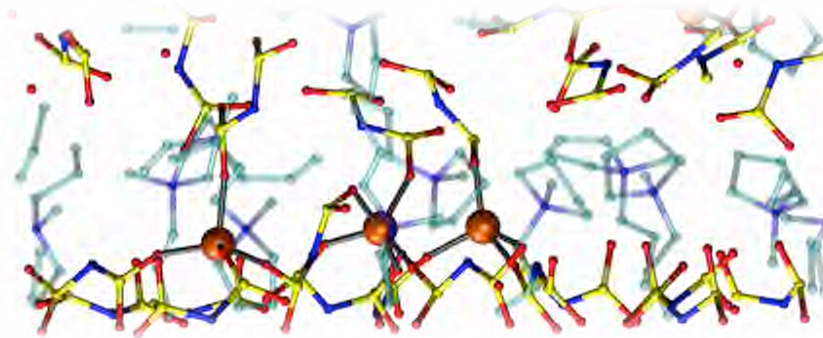
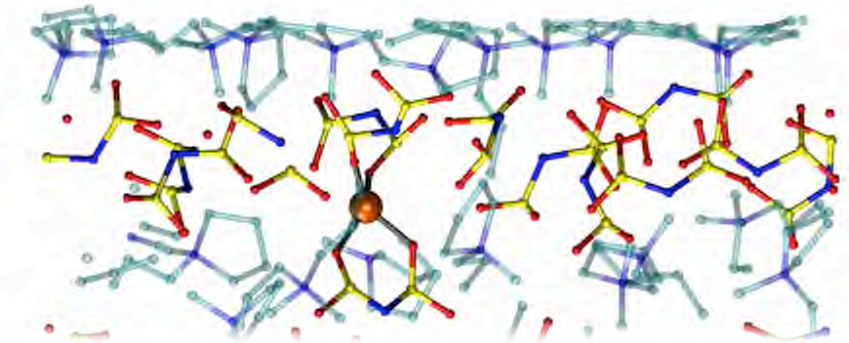


Li⁺ disrupts the EDL and accumulates in 2nd layer!

Li⁺ binding at the interface: [pyr14][TFSI]



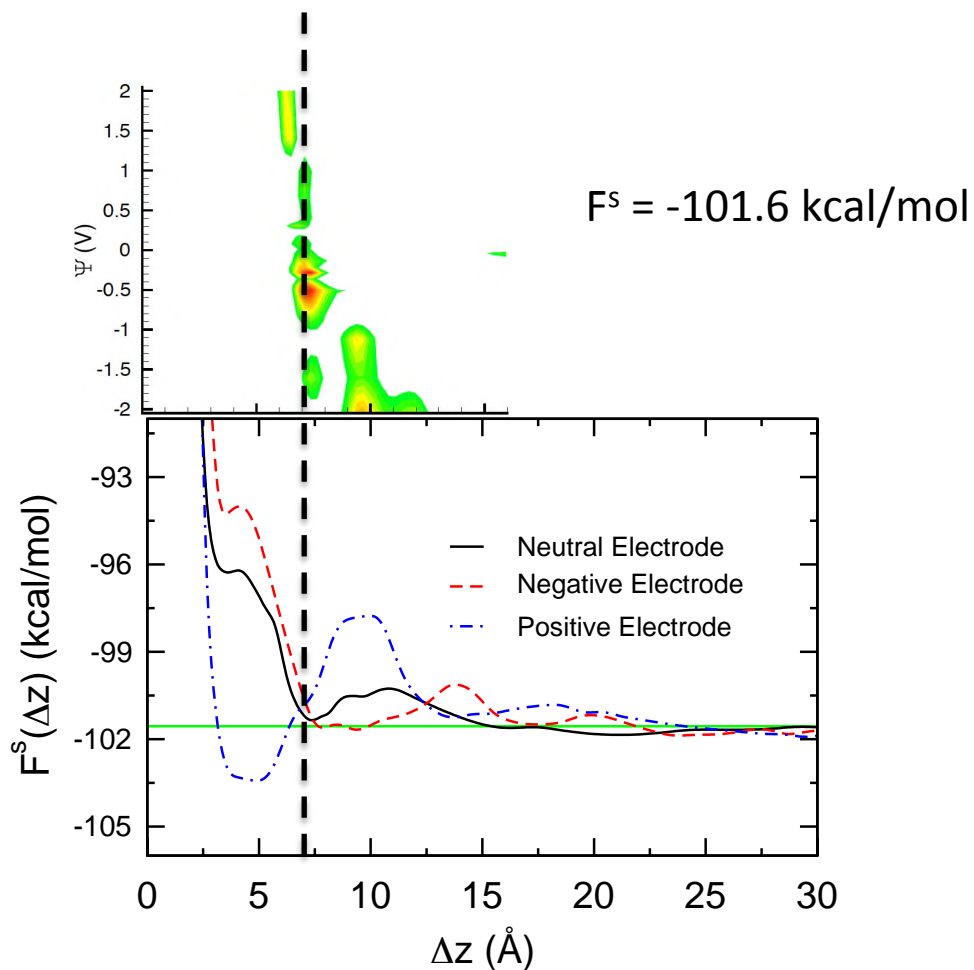
Anode



Cathode

Li⁺ accumulates in the second molecular layer!

Free energy barrier to Li^+ intercalation: [pyr14][TFSI]

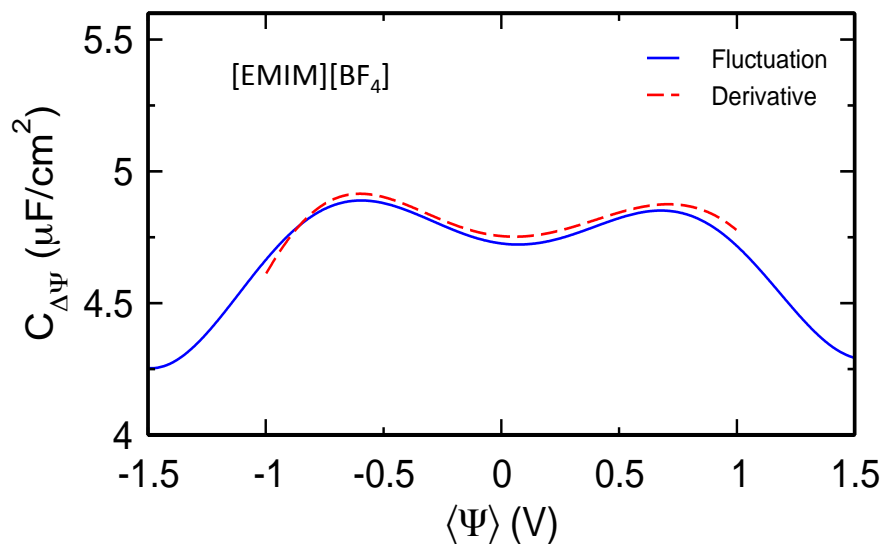


Solvation free energy concurs with Li-density!

Capacitance fluctuation formulas and electrode effects



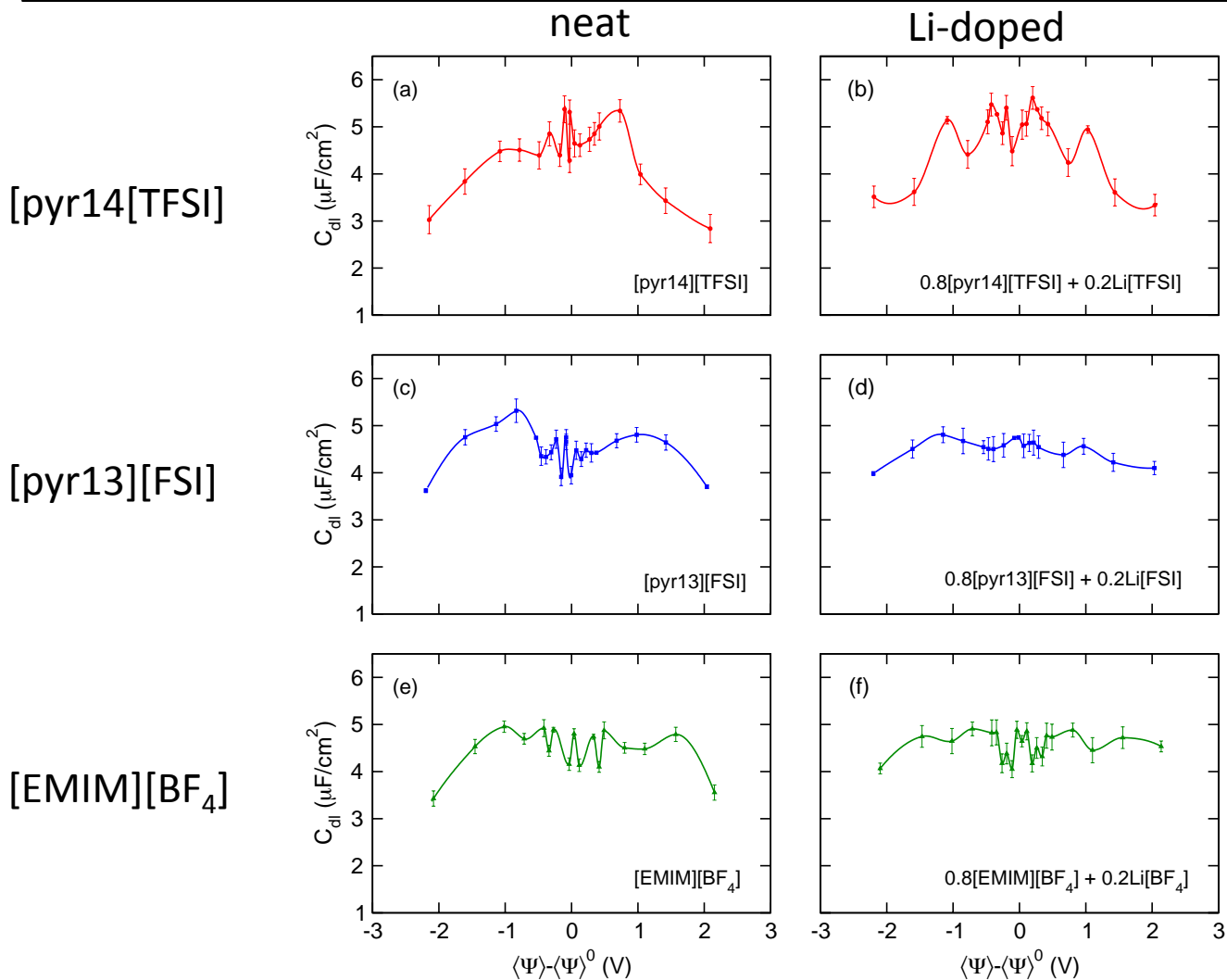
$$C_{\Delta\Psi} = \frac{\partial\langle\sigma\rangle}{\partial\langle\Psi\rangle} = \left[\beta A \langle|\sigma|\delta\sigma\rangle + \left\langle \frac{\partial\sigma}{\partial\Delta\Psi} \right\rangle \right] \left[\beta A \langle|\sigma|\delta\Psi\rangle + \left\langle \frac{\partial\Psi}{\partial\Delta\Psi} \right\rangle \right]^{-1}$$



Validated fluctuation formulas for capacitance!



Influence of Li^+ on capacitance



Computations performed on ideal graphite electrodes!

Specific energy estimate



		E (Wh/m ²)	E (Wh/kg)
[pyr14][TFSI]	Theory	0.7-1.3	0.8-1.4
	Exp.	1.4-3.5	1.5-3.8
[pyr13][FSI]	Theory	0.7-1.4	0.8-1.5
	Exp.	3.5-6.8	3.8-7.3
[EMIM][BF ₄]	Theory	0.5-0.9	0.5-1.0
	Exp.	1.3-1.5	1.4-1.6

Assume specific surface area 1074 m²/g

[pyr13][FSI] highest energy from both experiment and theory!

Conclusions



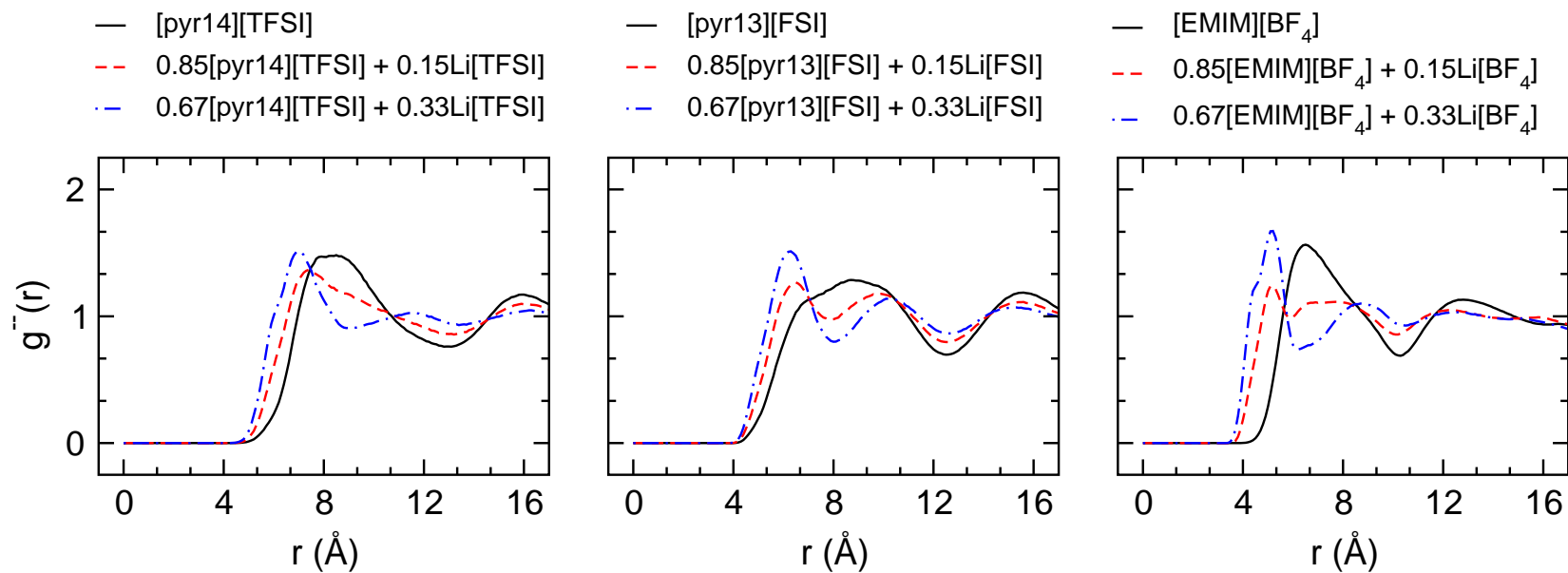
- **Computational study of Li-doped ILs with experimental validation**
- **Solvation structure identification through complimentary simulation approaches**
- **Influence of networks on experimental anion solvation number**
- **Bulk transport and electrochemical properties in good agreement with experiment**
- **Li⁺ disruption of the electric double layer**
- **Fluctuation formulas and camel-type shape of capacitance**
- **Future work: inclusion of more realistic interfacial effects to refine capacitance**

Additional Slides

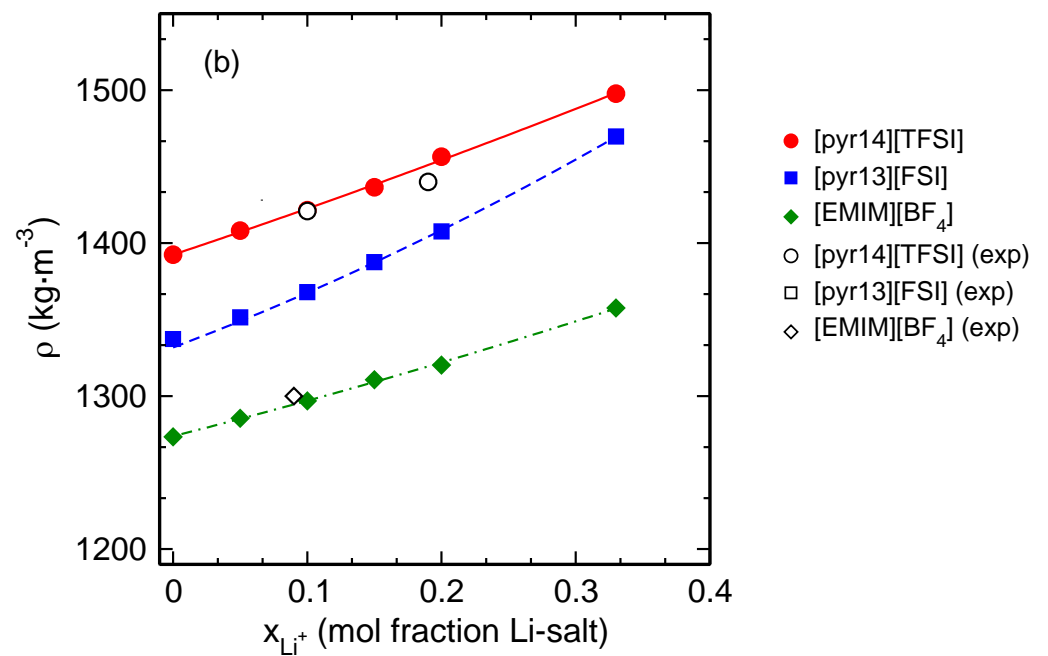
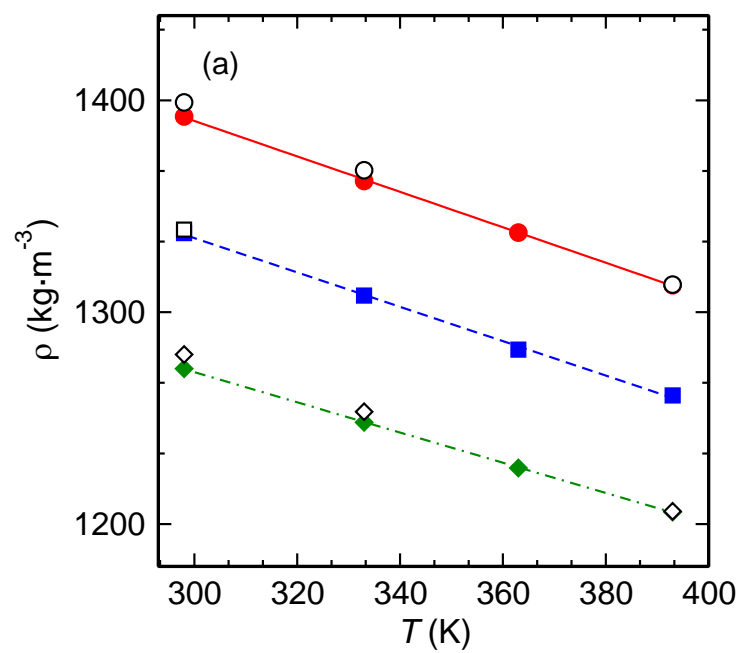
Influence of Li⁺-doping on anion distributions



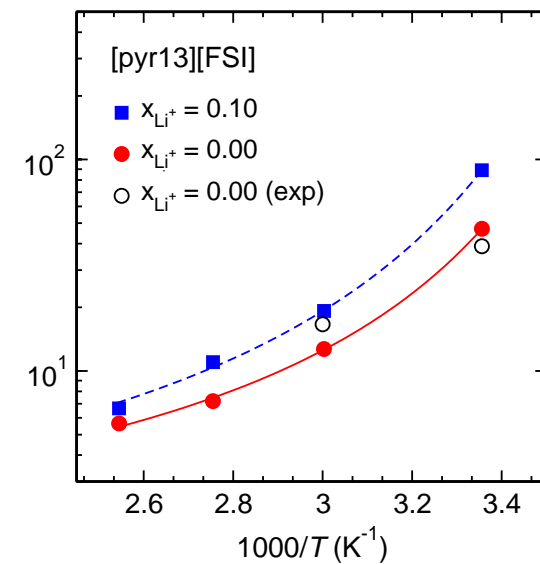
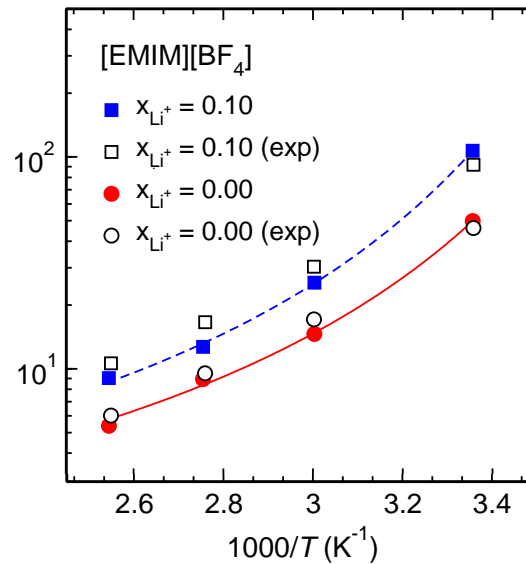
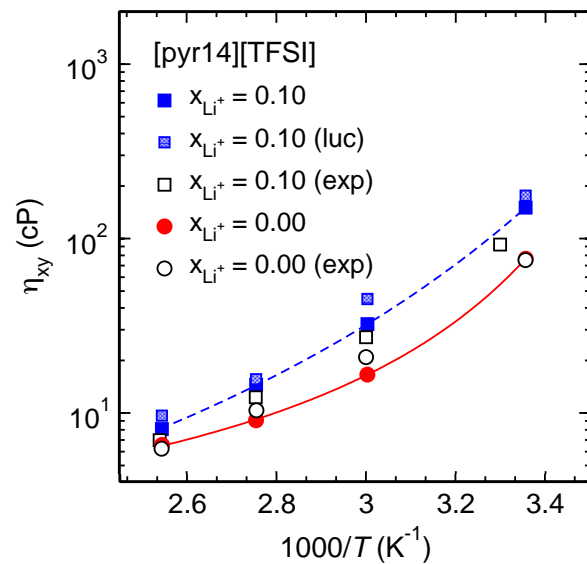
Small anion separation around Li⁺!



Density



Viscosity



Computational measures of thermodynamics and transport

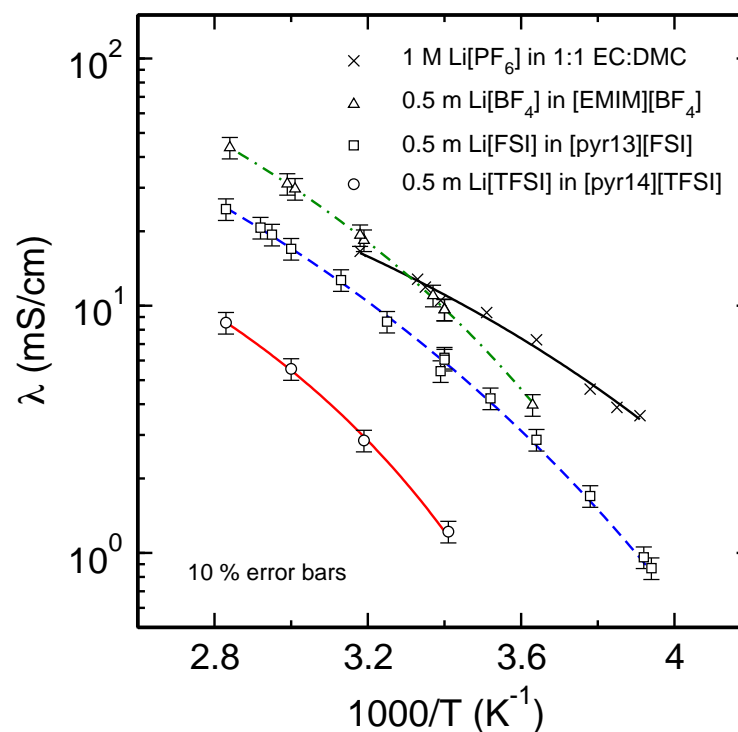


Density: ρ (kg/m³) | Diffusion: D (1e-10 m²/s) | Viscosity: μ (cP) | Conductivity: λ (mS/cm)

	[pyr14][TFSI]	[pyr13][FSI]	[EMIM][BF ₄]
ρ	1421.5	1367.9	1296.9
D^+	0.097	0.118	0.326
D^-	0.081	0.121	0.228
D^{Li}	0.046	0.069	0.101
μ	150	89	107
λ	1.67	3.35	11.45

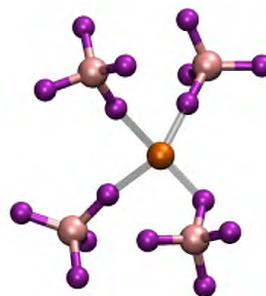
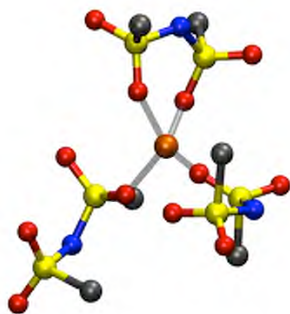
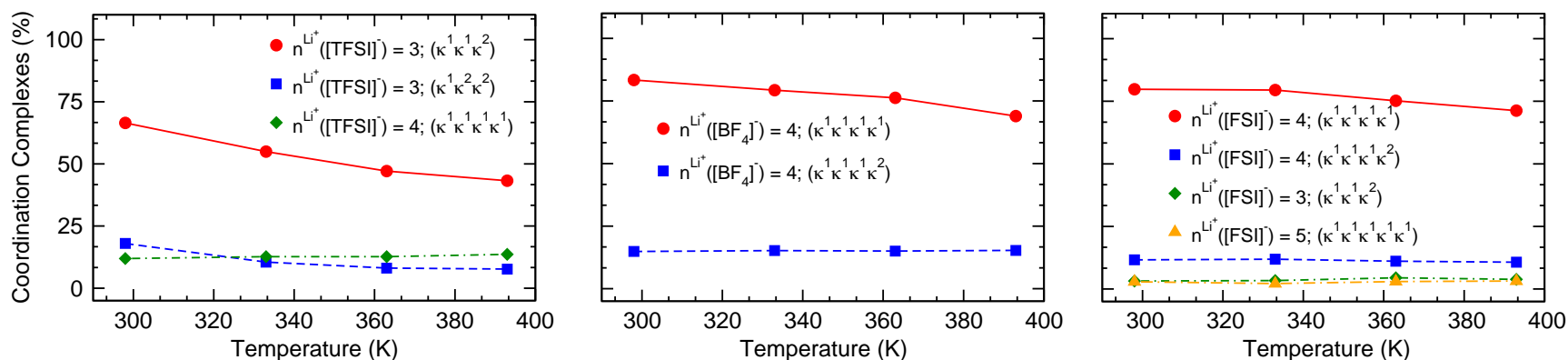
- " Greater ion mobility with decreasing density and ion size!
- " High accuracy of predicted properties:!
 - " density within ~1%!
 - " diffusion within 10-25%!
 - " conductivity within 10-20%!

Experimental comparison of ionic conductivity to that of Li-ion battery organic electrolytes



Mid-T ion conductivity comparable to conventional electrolytes!

Prevalent Li⁺/Anion solvation shells

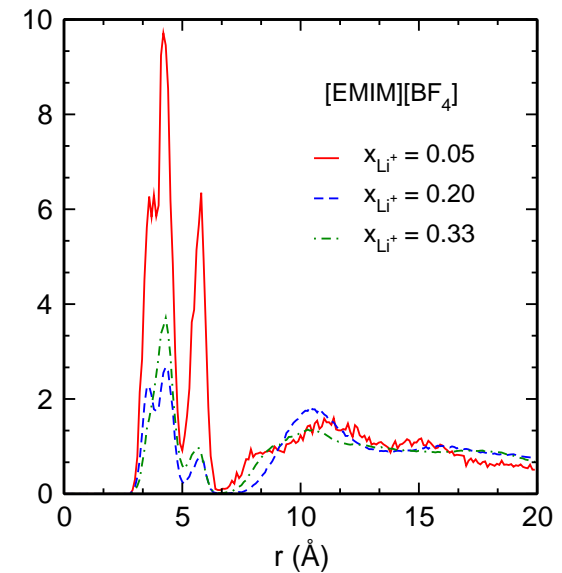
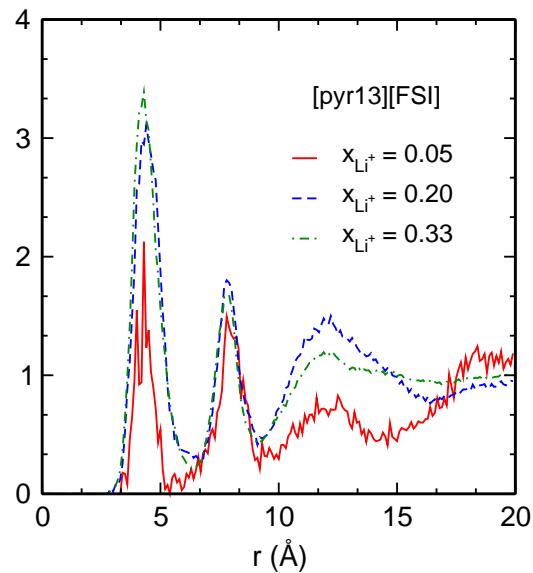
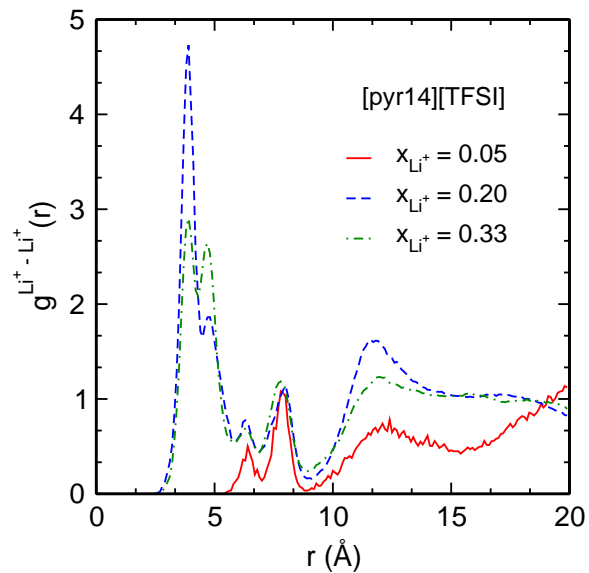


- 4-5 anion neighbors in Li⁺ solvation shell: [TFSI] (3-4), [BF₄] (4), [FSI] (3-5)!
- [Li(TFSI)₂]⁻ and [Li(FSI)₃]⁻² from experiment (J.C. Lassegues, et al., *J. Phys. Chem. A* **113**, 305 (2009) and K. Fujii, et al., *J. Phys. Chem. C* **117**, 19314 (2013))!

Li⁺-Li⁺ distributions



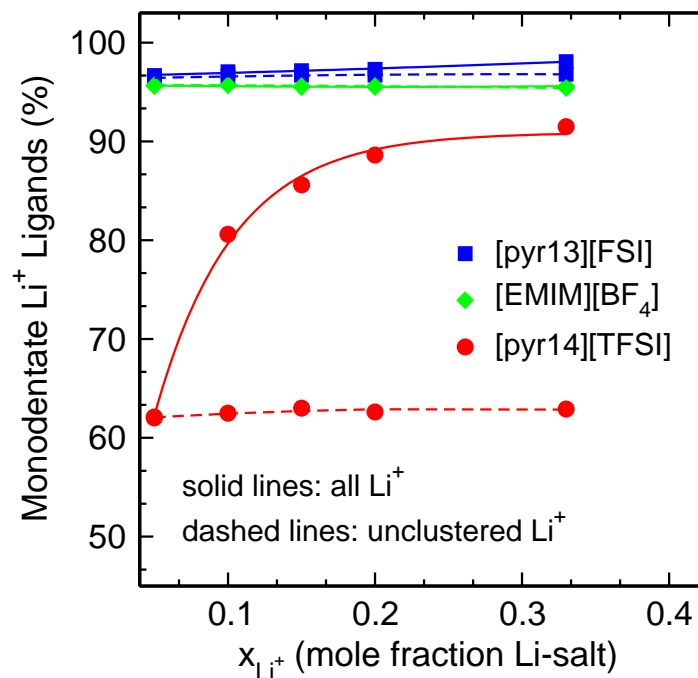
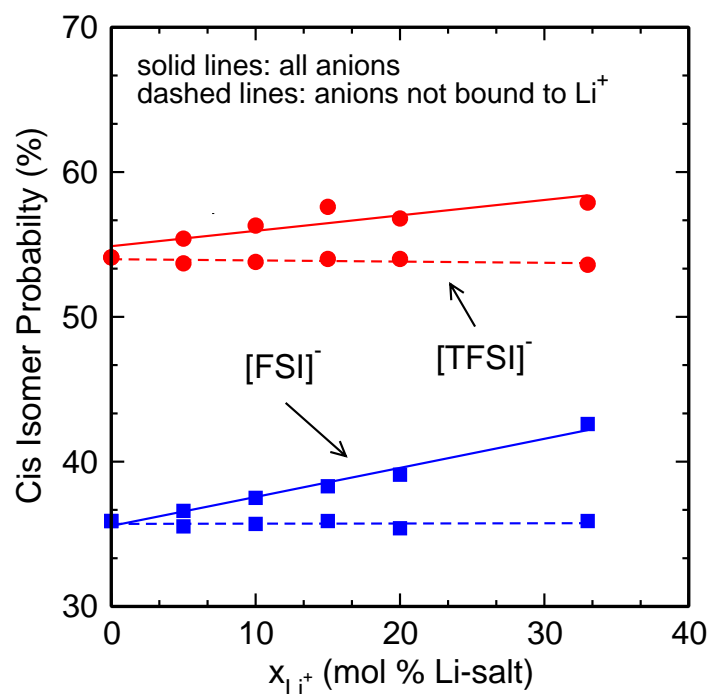
Li⁺ Li⁺ networks at most doping levels!



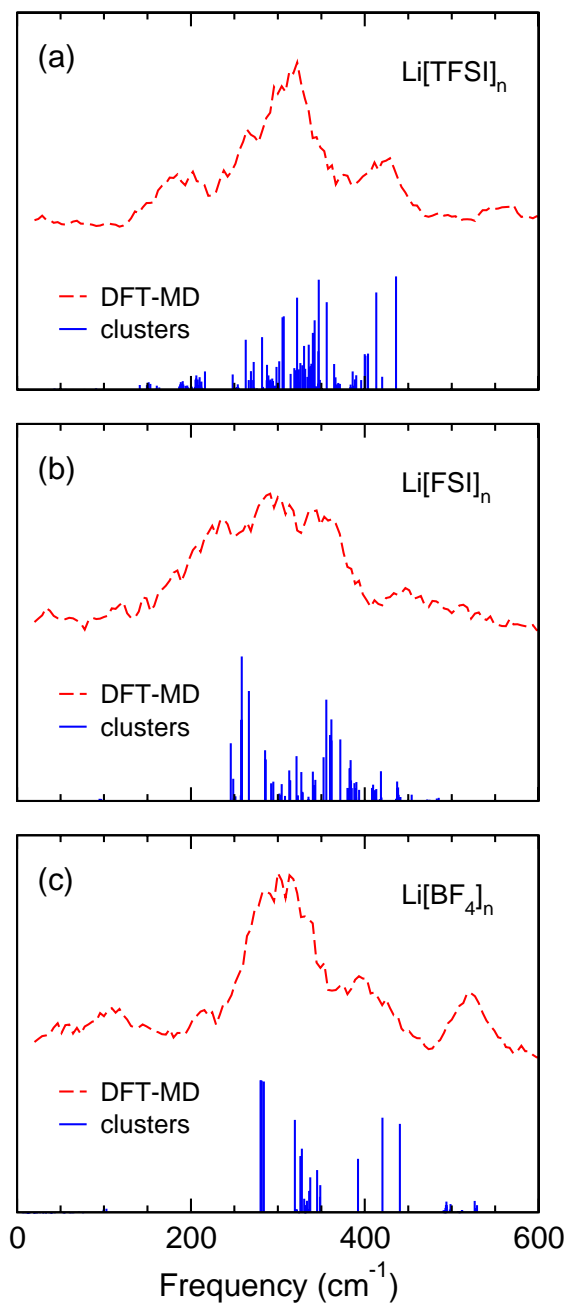
Influence of Li^+ ... Li^+ networks on structure



Li^+ Li^+ networks induce cis-conformers and monodentate bonds!



Solvation shells of L



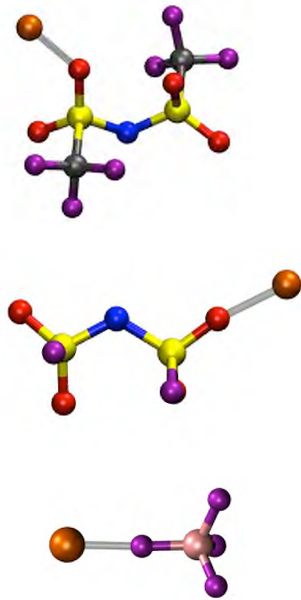
3 anion coord

'SI] and [BF₄]!

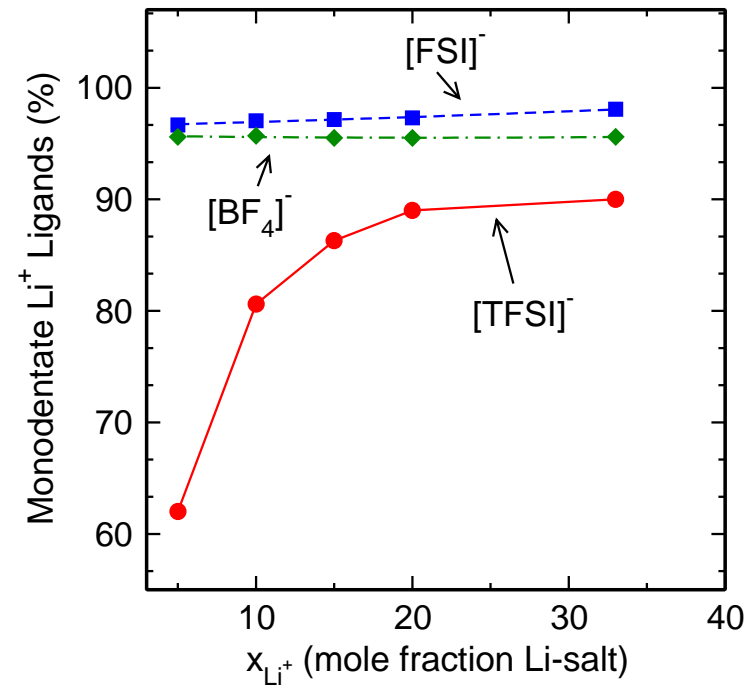
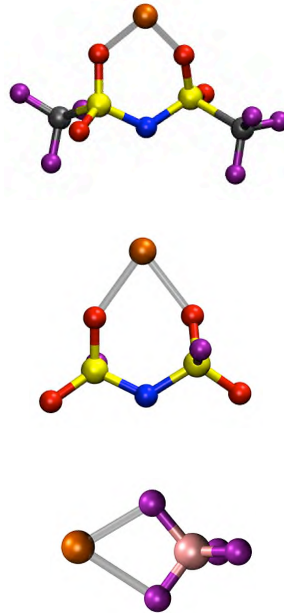
Li⁺/Anion bonding



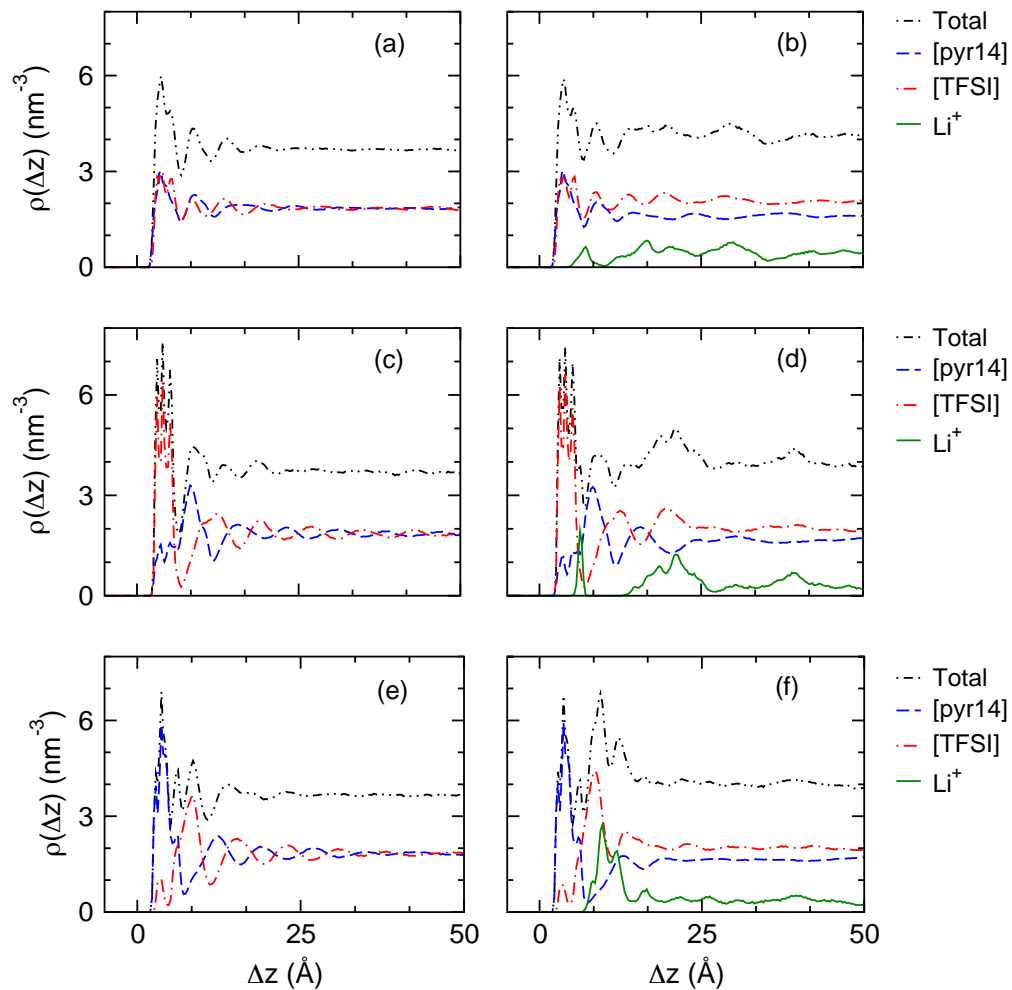
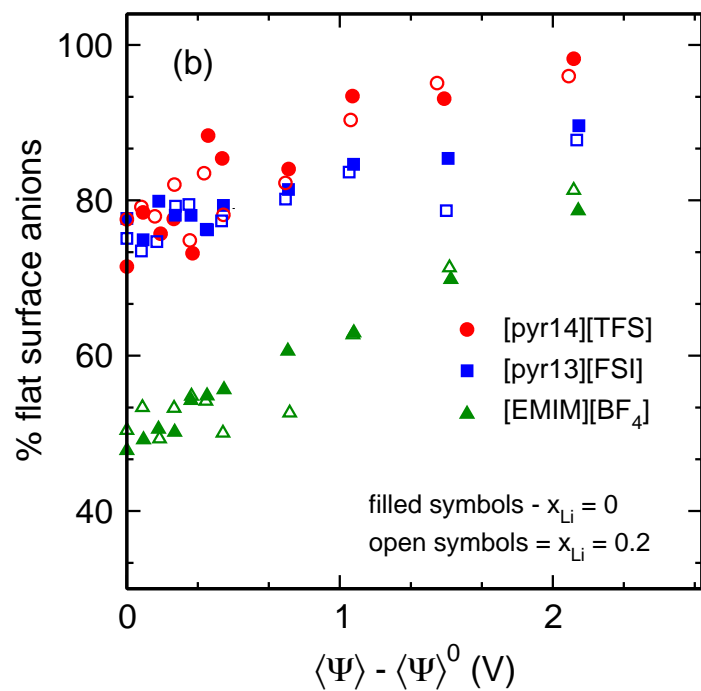
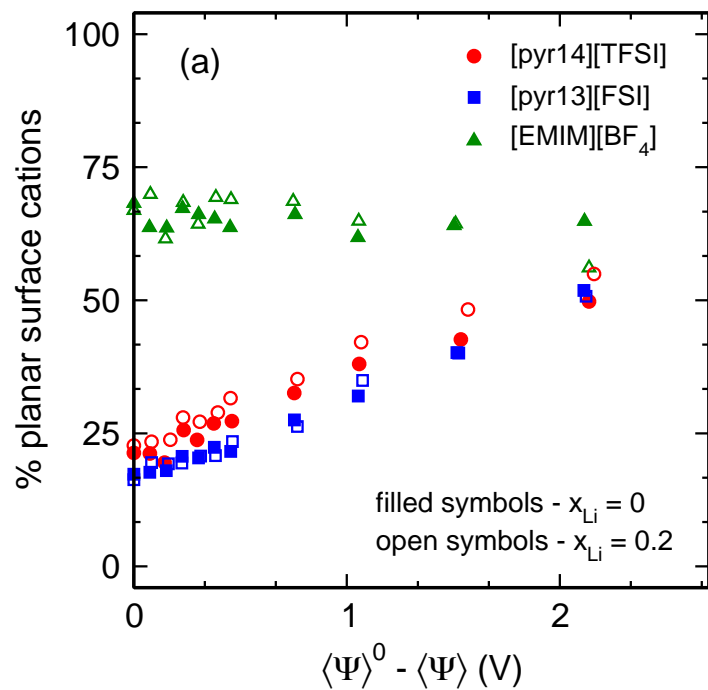
Monodentate (κ^1)



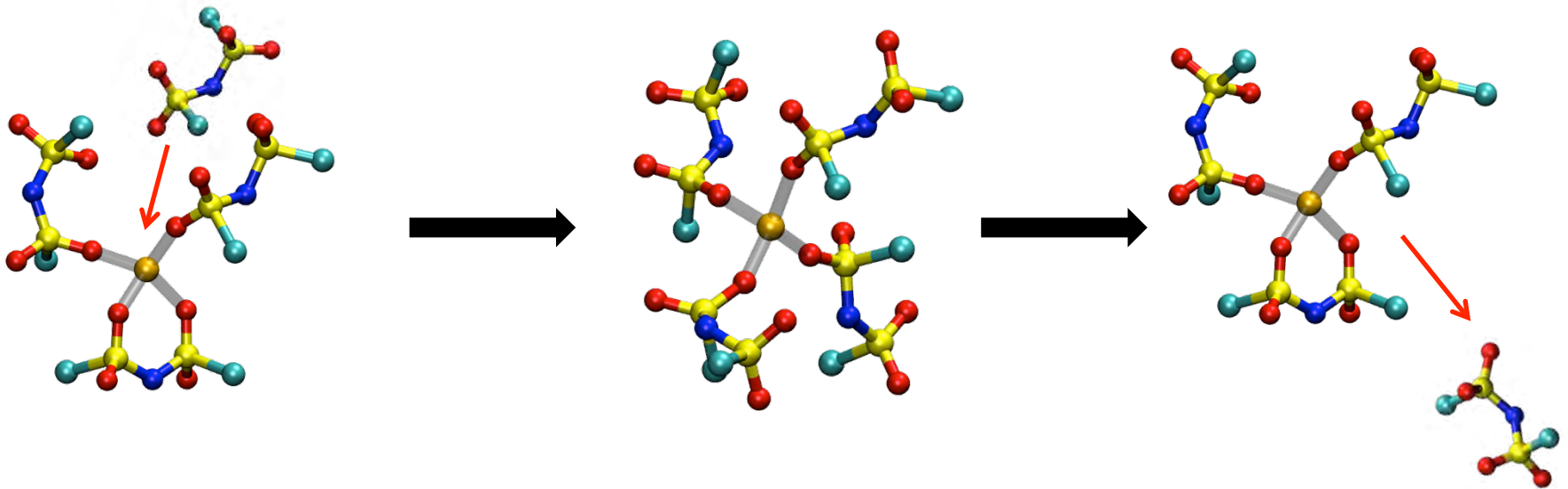
Bidentate (κ^2)



Monodentate bonding preferred at high Li-doping!



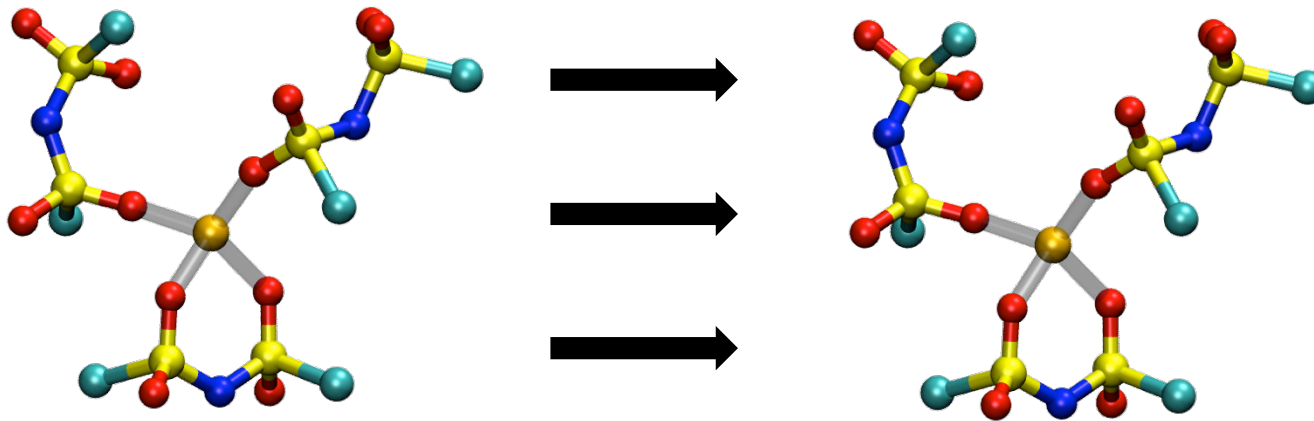
What is the mechanism for Li-diffusion?



Anion Exchange

Hopping of Li^+ through exchange of anions!

What is the mechanism for Li-diffusion?

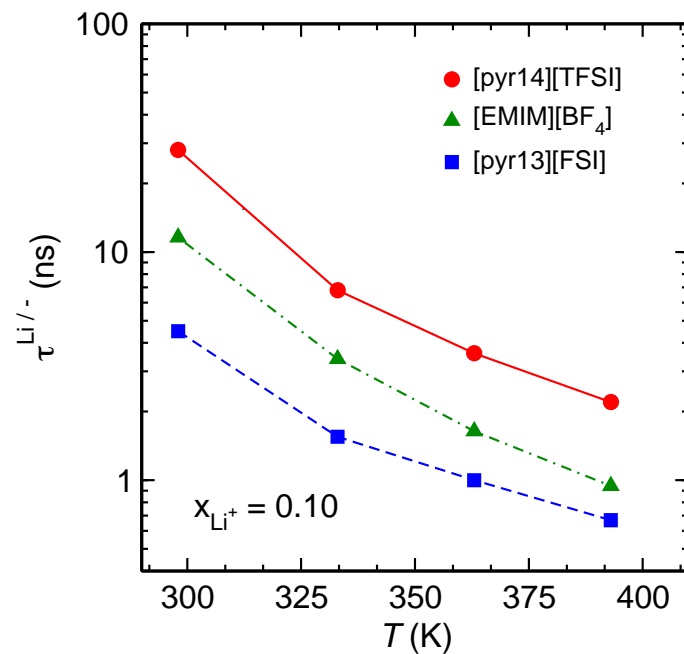
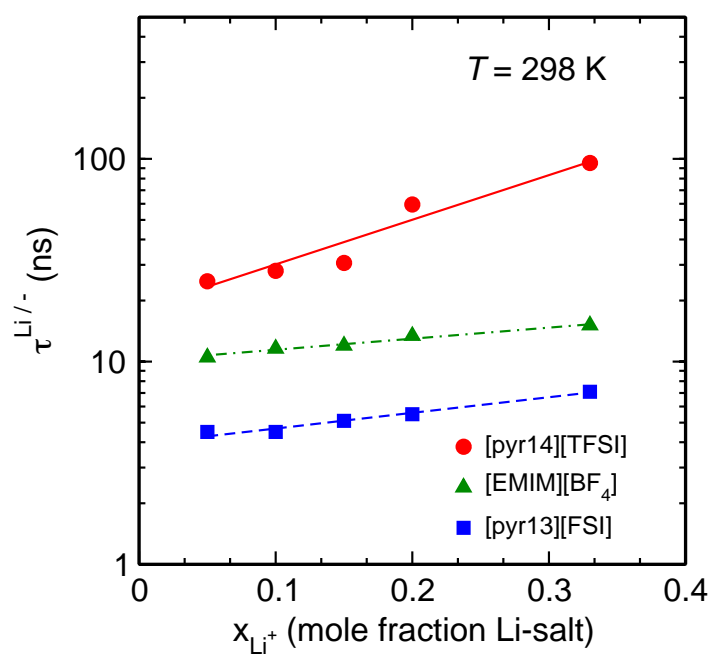


Vehicular

Net motion of Li^+ with the solvation shell!



Li⁺/Anion residence times



[TFSI] has longer residence times than other anions!

!

Note: residence time of [TFSI] 30 ns at room-T!

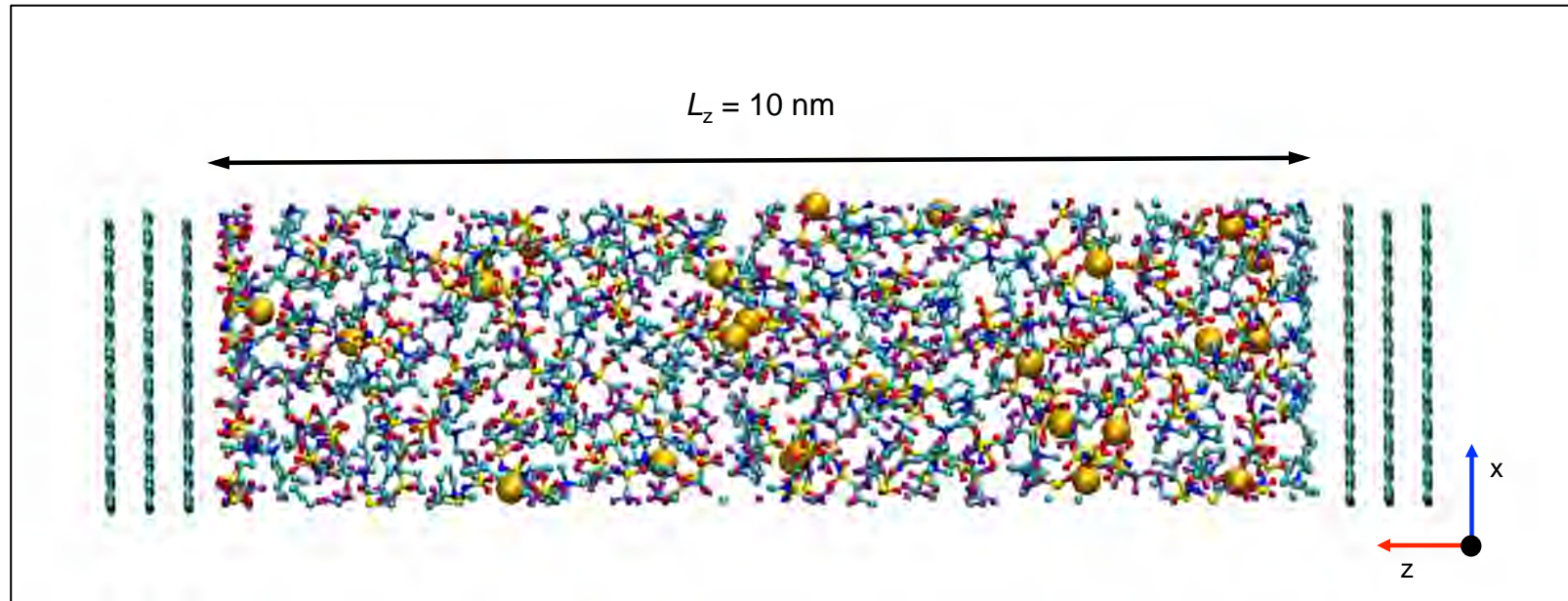
Room-T diffusion kinetics



	[pyr14][TFSI]	[pyr13][FSI]	[EMIM][BF ₄]
x_{Li}	D_{veh}/D_{tot}	D_{veh}/D_{tot}	D_{veh}/D_{tot}
0.05	0.69	0.81	0.89
0.10	0.66	0.85	1.07
0.33	0.59	0.73	0.91

Vehicular mechanism dominates the diffusion and increases in importance with decreasing anion size !

Interfacial Structure Simulations

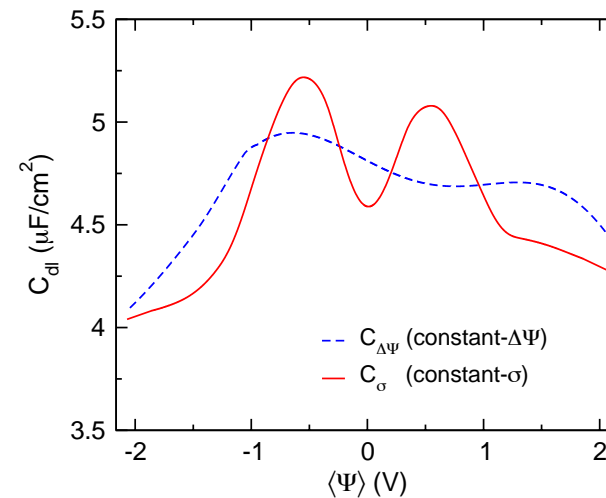
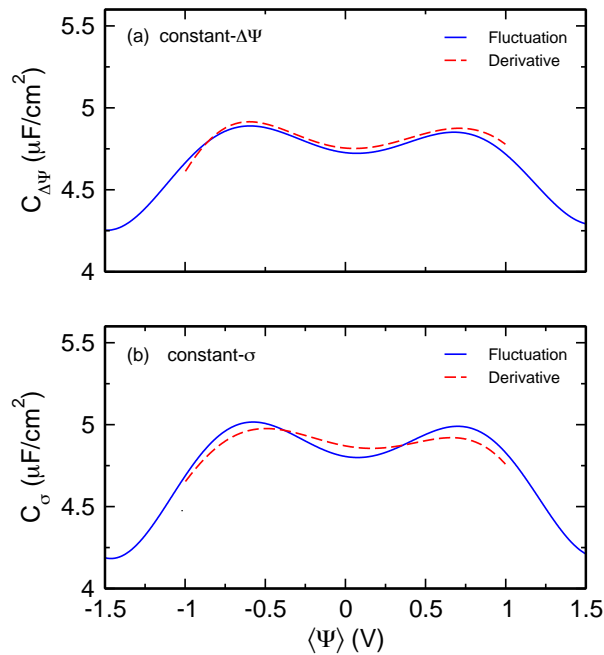


Two electrode simulations performed as a function of electrode voltage drop!

Capacitance fluctuation formulas and electrode effects



$$C_{\Delta\Psi} = \frac{\partial\langle\sigma\rangle}{\partial\langle\Psi\rangle} = \left[\beta A \langle|\sigma|\delta\sigma\rangle + \left\langle \frac{\partial\sigma}{\partial\Delta\Psi} \right\rangle \right] \left[\beta A \langle|\sigma|\delta\Psi\rangle + \left\langle \frac{\partial\Psi}{\partial\Delta\Psi} \right\rangle \right]^{-1}$$



Validated fluctuation formulas for capacitance!
Electrode surface subtly influences capacitance!

Diffusion



		t^{sim}	N_{pairs}	t	$D^{+,app}(t)$	$D^{-,app}(t)$	$D^{Li,app}(t)$
[pyr14][TFSI]	DFT-MD	0.1	8	0.05	6.47 (3.2)	6.10 (2.4)	1.91 (0.6)
	PFF-MD	6.0	8	0.05	4.23	3.17	0.75
		6.0	8	$t \rightarrow \infty$	1.40	0.89	0.28
		6.0	144	$t \rightarrow \infty$	0.80	0.66	0.34
[pyr13][FSI]	DFT-MD	0.1	8	0.05	4.78 (2.3)	4.27 (2.4)	1.64 (0.5)
	PFF-MD	6.0	8	0.05	4.85	3.85	0.92
		6.0	8	$t \rightarrow \infty$	1.41	1.29	0.44
		6.0	216	$t \rightarrow \infty$	0.89	0.91	0.47
[EMIM][BF ₄]	DFT-MD	0.1	8	0.05	7.77 (3.6)	3.78 (2.2)	1.03 (0.3)
	PFF-MD	6.0	8	0.05	4.77	2.97	0.97
		6.0	8	$t \rightarrow \infty$	1.97	1.48	0.75
		6.0	216	$t \rightarrow \infty$	1.93	1.38	0.65

Adjusting for time-scale and size effects brings DFT measure close to polarizable MD and experiment!

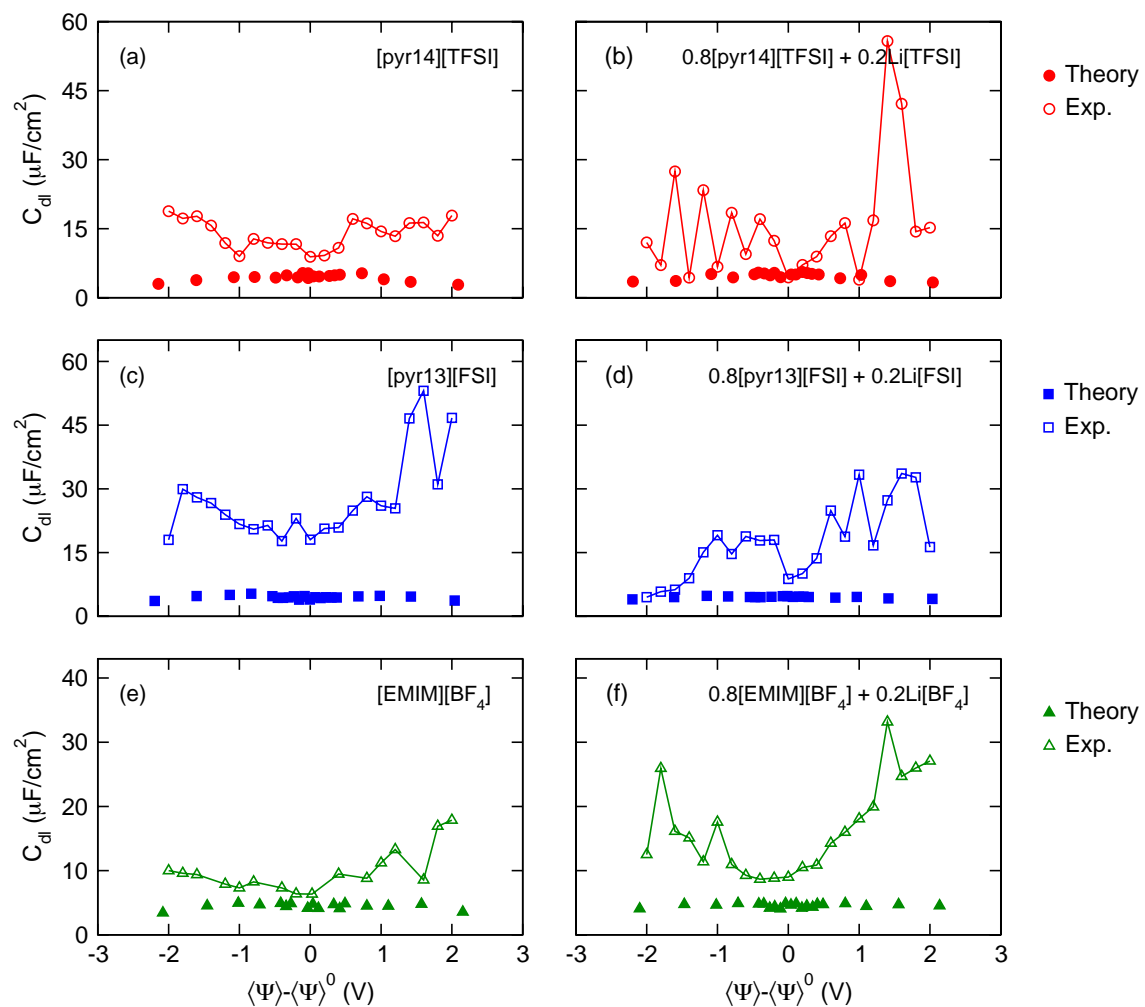
Surface energy estimate



		Elec. Window (eV)	C_{dl} (F/m ²)	E (Wh/m ²)
[pyr14][TFSI]	Theory	4.6-6.53	4.4	0.7-1.3
	Exp.	3.8-6	13.9	1.4-3.5
[pyr13][FSI]	Theory	4.7-6.4	4.5	0.7-1.4
	Exp.	4.3-6	27.2	3.5-6.8
[EMIM][BF ₄]	Theory	3.9-5.5	4.5	0.5-0.9
	Exp.	4.3-4.6	9.9	1.3-1.5

Experiments performed on glassy carbon!

Experimental analysis of capacitance



Experiments performed on glassy carbon!